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Preparation and Reactions of Tantalum Alkylidene Complexes
Containing Bulky Phenoxide or Thiolate Ligands.
Controlling Ring-Opening Metathesis Polymerization
Activity and Mechanism Through Choice of Anionic Ligand

by

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18. SUBJECT TERMS

Tantalum alkylidene complexes	Wittig-like reactivity
Bulky phenoxide ligands	Acyclic olefins
2,6-diisopropylphenoxide ligands (DIPP)	Strained cyclic olefins
Bulky thiolate ligands	Ring-opening metathesis polymerization (ROMP)
2,4,6-triisopropylbenzenethiolate ligands (TIPT)	Norbornene (NBE)
Reactivity of phenoxide vs. thiolate ligands	Living polymers
Tantalacyclobutane complexes	Low polydispersities
Distorted square pyramidal geometry	Some secondary metathesis
Trigonal bipyramidal geometry	Polymer cleaved from metal with benzaldehyde
Oxytantalacyclohexene complexes	Kinetics of polymerizations

19. ABSTRACT

Addition of LiDIPP (DIPP = 0-2,6-C₆H₃iPr₂) to Ta(CH^tBu)(THF)₂Cl₃ yields Ta(CH^tBu)(DIPP)₃(THF) (1) in high yield. Ta(CH^tBu)(DMP)₃(THF) (3; DMP = 0-2,6-C₆H₃Me₂) and Ta(CH^tBu)(TIPT)₃(THF) (5; TIPT = S-2,4,6-C₆H₂iPr₃) can be prepared by analogous methods. 1 reacts rapidly with one eq of styrene to give the tantalacyclobutane complex Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃. Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃ belongs to the space group P2₁/n with $a = 21.338(11)$ Å, $\beta = 11.699(5)$ Å, $c = 37.198(23)$ Å, $b = 102.66(5)^\circ$, $Z = 8$, M_r 887.03 g, $V = 9060.1$ Å³, $\rho(\text{calcd}) = 1.301$ g cm⁻³. The overall structure is a distorted square pyramid. The TaC₃ ring is slightly bent (25.2°) with the phenyl and t-butyl groups *trans* to one another. The TaC₃ ring is elongated in the Ta...C_β direction compared to trigonal bipyramidal tantalacycle and tungstacycle complexes in which the MC₃ ring is bound in equatorial positions. An analogous reaction between 1 and vinyltrimethylsilane gives Ta(CHSiMe₃)(DIPP)₃(THF) or Ta[CH(SiMe₃)CH(SiMe₃)CH₂](DIPP)₃ depending upon reaction conditions; the two are in ready equilibrium. 1 reacts smoothly with ethylene to give Ta(CH₂CH₂CH₂)(DIPP)₃ in high yield, but treatment of 1 with olefins such as propylene or 1-butene did not lead to any characterizable species. Addition of excess *cis*-2-pentene to 1 results in rapid metathesis (100 eq to equilibrium in <15 m), but activity is short-lived. In contrast to reactions between 1 and olefins, Ta(CH^tBu)(TIPT)₃(THF) does not react with ordinary olefins, and will not metathesize them. Tantalacyclobutane complexes containing the DIPP ligand react with the carbonyl functionality to give a mixture of insertion chemistry (oxytantalacyclohexene complexes) and Wittig-like reactivity, depending upon the carbonyl compound, the tantalacycle, and the temperature. 1 reacts with norbornene to give an isolable tantalacyclobutane complex, Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃, a crystal structure study of which showed it to be a trigonal bipyramidal species analogous to W[CH(SiMe₃)CH(SiMe₃)CH₂](N-2,6-C₆H₃iPr₂)[OCMe(CF₃)₂]₂. (Crystal data are space group P2₁/n, $a = 11.587(4)$ Å, $b = 20.795(4)$ Å, $c = 18.388(4)$ Å, $V = 4416.6$ Å³, $Z = 4$, M_r 877.03 g, $\rho(\text{calcd}) = 1.319$ g cm⁻³.) Norbornene is polymerized by Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃ in a reaction that is zero order in norbornene (characteristic of rate-limiting opening of the TaC₃ ring followed by rapid capture of the incipient alkylidene complex by NBE) until ~1 equivalent of NBE remains, at which point it becomes first order in NBE. Analogous reactions between Ta(CH^tBu)(TIPT)₃(py) and NBE are first order in NBE, and loss of pyridine is required. The living polymer in the TIPT case is an alkylidene complex. In each system the polymer can be cleaved from the metal with benzaldehyde and shown to be monodisperse. Only in the TIPT system is secondary metathesis (after NBE has been consumed) negligible.

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Abstract

Addition of LiDIPP (DIPP = 0-2,6-C₆H₃ⁱPr₂) to Ta(CH^tBu)(THF)₂Cl₃ yields Ta(CH^tBu)(DIPP)₃(THF) (1) in high yield. Ta(CH^tBu)(DMP)₃(THF) (3; DMP = 0-2,6-C₆H₃Me₂) and Ta(CH^tBu)(TIPT)₃(THF) (5; TIPT = S-2,4,6-C₆H₂ⁱPr₃) can be prepared by analogous methods. 1 reacts rapidly with one eq of styrene to give the tantalacyclobutane complex Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃. Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃ belongs to the space group P2₁/n with *a* = 21.338(11) Å, *b* = 11.699(5) Å, *c* = 37.198(23) Å, β = 102.66(5)°, *Z* = 8, *M_r* 887.03 g, *V* = 9060.1 Å³, ρ(calcd) = 1.301 g cm⁻³. The overall structure is a distorted square pyramid. The TaC₃ ring is slightly bent (25.2°) with the phenyl and t-butyl groups *trans* to one another. The TaC₃ ring is elongated in the Ta...C_β direction compared to trigonal bipyramidal tantalacycle and tungstacycle complexes in which the MC₃ ring is bound in equatorial positions. An analogous reaction between 1 and vinyltrimethylsilane gives Ta(CHSiMe₃)(DIPP)₃(THF) or



$\text{Ta}[\text{CH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{CH}_2](\text{DIPP})_3$ depending upon reaction conditions; the two are in ready equilibrium. **1** reacts smoothly with ethylene to give $\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{DIPP})_3$ in high yield, but treatment of **1** with olefins such as propylene or 1-butene did not lead to any characterizable species. Addition of excess *cis*-2-pentene to **1** results in rapid metathesis (100 eq to equilibrium in < 15 m), but activity is short-lived. In contrast to reactions between **1** and olefins, $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{THF})$ does not react with ordinary olefins, and will not metathesize them. Tantalacyclobutane complexes containing the DIPP ligand react with the carbonyl functionality to give a mixture of insertion chemistry (oxytantalacyclohexane complexes) and Wittig-like reactivity, depending upon the carbonyl compound, the tantalacycle, and the temperature. **1** reacts with norbornene to give an isolable tantalacyclobutane complex, $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}^t\text{Bu}](\text{DIPP})_3$, a crystal structure study of which showed it to be a trigonal bipyramidal species analogous to $\text{W}[\text{CH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{CH}_2](\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$. (Crystal data are space group $\text{P}2_1/n$, $a = 11.587(4)$ Å, $b = 20.795(4)$ Å, $c = 18.388(4)$ Å, $V = 4416.6$ Å³, $Z = 4$, M_r 877.03 g, $\rho(\text{calcd}) = 1.319$ g cm⁻³.) Norbornene is polymerized by $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}^t\text{Bu}](\text{DIPP})_3$ in a reaction that is zero order in norbornene (characteristic of rate-limiting opening of the TaC_3 ring followed by rapid capture of the incipient alkylidene complex by NBE) until ~ 1 equivalent of NBE remains, at which point it becomes first order in NBE. Analogous reactions between $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{py})$ and NBE are first order in NBE, and loss of pyridine is required. The living polymer in the TIPT case is an alkylidene complex. In each system the polymer can be cleaved from the metal with benzaldehyde and shown to be monodisperse. Only in the TIPT system is secondary metathesis (after NBE has been consumed) negligible.

INTRODUCTION

We have reported a variety of high oxidation state, electronically unsaturated alkylidyne¹ and (more recently) alkylidene² complexes of tungsten and molybdenum that contain bulky alkoxide ligands. Examples are $\text{W}(\text{CR})(\text{O}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)_3$,^{1b} $\text{Mo}(\text{CR})[\text{OCMe}(\text{CF}_3)_2]_3$,^{1c} $\text{W}(\text{CHR})(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$,^{2b} and $\text{Mo}(\text{CHR})(\text{N}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$.^{2c} It is becoming clear that bulky alkoxide ligands not only can protect a four- or five-coordinate metal

complex against deleterious bimolecular decomposition reactions, but also can closely control the reactivity of the metal complex in acetylene^{1a,3} and olefin⁴ metathesis reactions.⁵ For example, $W(CHR)(N-2,6-C_6H_3^iPr_2)[OCMe(CF_3)_2]_2$ complexes are extremely efficient olefin metathesis catalysts (lower limit $\sim 10^3$ turnovers of *cis*-2-pentene per minute at 25°)^{2b} while $W(CHR)(N-2,6-C_6H_3^iPr_2)(O^tBu)_2$ is *virtually inactive* as a metathesis catalyst for *cis*-2-pentene.⁴ $(M(CHR)(N-2,6-C_6H_3^iPr_2)(O^tBu)_2)$ complexes ($M = Mo$ or W) will react with strained olefins such as norbornene, a fact that makes them extremely useful as catalysts for controlled ring-opening metathesis reactions⁸ to give monodisperse polymers.^{4,7)}

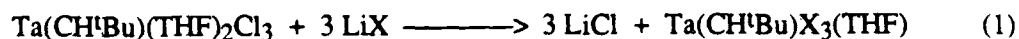
We decided to test whether some of the principles we had uncovered in tungsten and molybdenum chemistry could be used to advantage in tantalum chemistry, especially since $Ta(CH^tBu)(THF)_2Cl_3$ can be prepared in high yield in two relatively easy steps from $TaCl_5$.⁹ Tantalum alkylidene complexes have been useful for outlining the principles of olefin metathesis,^{10,11} but none has been long-lived enough to be practical for metathesis of ordinary olefins. Therefore we felt we had a better chance of preparing reagents for Wittig-like reactions¹² or catalysts for the controlled ring-opening of strained cyclic olefins.^{4,7,13} We also wanted to compare various other supporting ligand systems with alkoxides in order to uncover major differences that might be useful in controlling metathesis activity. In this paper we report the preparation and a comparison of the reactivity of complexes of the type $Ta(CH^tBu)X_3(THF)$ where X is a bulky phenoxide or phenyl thiolate ligand. We have found that differences between phenoxide and phenyl thiolate systems are dramatic; the choice determines both activity and mechanism. Some of these results have been reported in preliminary form.¹⁴

RESULTS

Preparation and Wittig-like Reactions of DIPP, DMP, and TIPT Neopentylidene Complexes.

Yellow $Ta(CH^tBu)(DIPP)_3(THF)$ (1; equation 1; DIPP = 2,6-diisopropylphenoxide) is formed in high yield upon treating isolated $Ta(CH^tBu)(THF)_2Cl_3$ ⁹ with 3 eq of LiDIPP. It also can be prepared from $Ta(CH^tBu)(THF)_2Cl_3$ that has been generated *in situ* in ether by addition of

excess THF to $\text{Ta}(\text{CH}^t\text{Bu})_2\text{Cl}_3$, although yields are comparable to those employing isolated

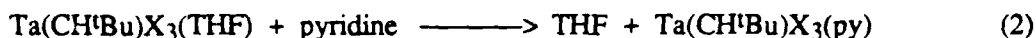


1; X = DIPP

3; X = DMP

5; X = TIPT

$\text{Ta}(\text{CH}^t\text{Bu})(\text{THF})_2\text{Cl}_3$ only when the reaction is performed on a small scale (< 5 g). $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ appears to be stable as a solid (under dinitrogen), but it decomposes slowly over a period of several days in C_6D_6 . We have not been able to remove THF from 1 in the solid state *in vacuo* at 25°, and it begins to decompose when heated. An analogous pyridine adduct (2; equation 2) is easily prepared by treating 1 with several equivalents of pyridine. Note



2; X = DIPP

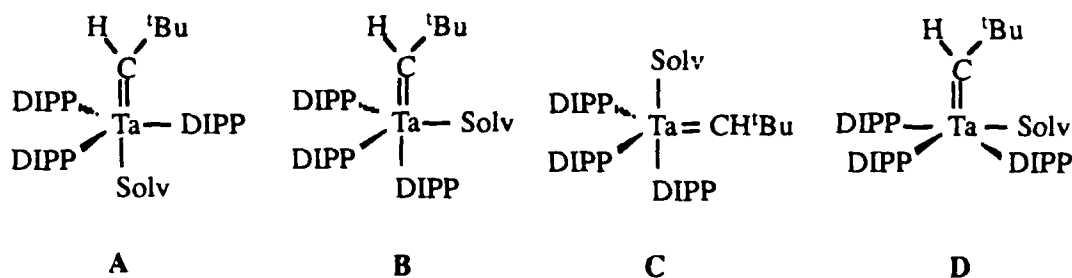
4; X = DMP

6; X = TIPT

that $\text{Ta}(\text{CH}^t\text{Bu})(\text{O}^t\text{Bu})_3$, the only other example of a $\text{Ta}(\text{CH}^t\text{Bu})(\text{OR})_3$ complex, is base-free, could not be isolated as a solid, and is unstable in solution.¹⁰

The ^1H and ^{13}C NMR spectra of 1 and 2 show the expected neopentylidene H_α resonances at 5.73 and 6.29 ppm, and C_α resonances at 227.1 and 231.2 ppm, respectively (Table I). The relatively low values for J_{CH} (95 and 96 Hz, respectively) suggest that the neopentylidene ligand in each case is distorted,¹¹ with a $\text{Ta}=\text{C}_\alpha-\text{C}_\beta$ angle of perhaps 150-160°. The DIPP resonances in 1 are relatively sharp at 25° in C_6D_6 but become broader and more complex as a sample (in toluene- d_8) is cooled. When 6 equivalents of THF are added to a sample of 1 in C_6D_6 , rapid exchange of coordinated THF with free THF is evident in the ^1H NMR spectrum at 25°. The DIPP resonances in the NMR spectrum of 2 at 25° are broader than they are in 1 at 25°. Four likely structures for 1 (we assume for now that the structure of 2 is analogous) are A through D (Solv = THF or pyridine). If the structure is of type A then the broadening of the DIPP signals

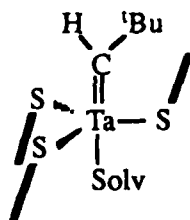
(observed at low temperature for **1** and at 25° for **2**) must be the result of a slowing down of rotation of the phenyl rings about the C-O bonds for steric reasons. If the structures are of type **B**, **C**, or **D**, then the broadening of the DIPP resonances can be attributed largely to the fact that two types of DIPP ligands are present in the static structure where Solv is held tightly. We favor **C**, since the geometry about the metal is analogous to that in $[\text{Ta}(\text{DIPP})_3(\text{THF})]_2(\mu\text{-N}_2)^{15\text{a}}$ and to that in the alkylidene complex, $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}^t\text{Bu}](\text{DIPP})_3(\text{py})$.^{15b}



$\text{Ta}(\text{CH}^t\text{Bu})(\text{DMP})_3(\text{THF})$ (**3**; equation 1; DMP = 2,6-dimethylphenoxide) can be prepared by treating $\text{Ta}(\text{CH}^t\text{Bu})(\text{THF})_2\text{Cl}_3$ with 3 eq of LiDMP, but the yield is lower than that of **1**. Surprisingly, **3** is less crystalline, more soluble in hydrocarbons, and significantly less stable in hydrocarbons than **1**. The reasons for the instability of **3** are unclear. One possibility is that the major decomposition pathway of $\text{Ta}(\text{CH}^t\text{Bu})(\text{OAr})_3(\text{THF})$ complexes is intermolecular, and that therefore they decompose more rapidly when OAr is a relatively small phenoxide. (In a related system, Rothwell and Chamberlain¹⁶ observed formation of $\text{Ta}(\text{O-2,6-C}_6\text{H}_3^t\text{Bu}_2)_2(\text{CH}_2)(\text{CH}_3)$ upon irradiation of $\text{Ta}(\text{O-2,6-C}_6\text{H}_3^t\text{Bu}_2)_2(\text{CH}_3)_3$, but although methane was observed upon irradiation of $\text{Ta}(\text{O-2,6-C}_6\text{H}_3\text{Me}_2)_2(\text{CH}_3)_3$ (indicative of α -hydride abstraction), no analogous methylene species was observed. They suggested that a methylene complex forms (possibly $\text{Ta}(\text{DMP})_2(\text{CH}_2)(\text{CH}_3)$), but that it decomposes much more rapidly than $\text{Ta}(\text{O-2,6-C}_6\text{H}_3^t\text{Bu}_2)_2(\text{CH}_2)(\text{CH}_3)$.) A pyridine adduct (**4**; equation 2) can be prepared straightforwardly by treating **3** with pyridine, but like **3**, **4** does not analyze well, we believe because of some slow decomposition in the solid state. The ^1H and ^{13}C NMR spectra of **3** and **4** are similar to those for

1 and **2** (Table I). Because of the instability and poor physical properties of **3**, we have not investigated DMP complexes in as much depth as DIPP complexes.

$\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{THF})$ (**5**; equation 1; $\text{TIPT} = 2,4,6\text{-triisopropylbenzenethiolate}$) can be prepared by treating $\text{Ta}(\text{CH}^t\text{Bu})(\text{THF})_2\text{Cl}_3$ with 3 eq of LiTIPT in ether. (A byproduct that is formed in small amounts is believed to be $[\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3]_2$; details may be found in the Experimental Section.) $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{py})$ (**6**) is prepared straightforwardly from $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{THF})$. Both **5** and **6** are stable as solids, but **5** appears to decompose slowly in C_6D_6 at 25° . The ^1H NMR spectrum of **5** at 25° displays resonances for only one type of thiolate ligand. Since the THF ligand in **5** is demonstrably exchanging rapidly with free THF at 25° (by ^1H NMR), and since the ^1H NMR spectrum of **6** displays broad TIPT resonances, we believe the TIPT ligands are inequivalent in both **5** and **6**. In all structurally characterized examples of TBP complexes that contain three bulky arylthiolate ligands the thiolates are found in equatorial positions with one pointed toward one axial ligand, and two toward the other axial ligand ("two down, one up") with M-S-C angles of $\sim 110^\circ$.^{15a,17,18} One of the members of this list is $[\text{Ta}(\text{S-2,6-C}_6\text{H}_3^i\text{Pr}_2)_3(\text{THF})]_2(\mu\text{-N}_2)$.^{15a} Therefore we propose that the structures of **5** and **6** are as shown (**E**), and that rotation about Ta-S bonds is slow. The TIPT ligands become



E

equivalent when solvent is lost to give $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3$, although the equilibrium between (e.g.) **5** and $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3$ must lie far towards **5** in order to slow down the formation of $[\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3]_2$ (see Experimental Section). Analogous results were observed in complexes of the type $\text{M}(\text{C}^t\text{Bu})(\text{TIPT})_3$ ($\text{M} = \text{Mo}$ or W).¹⁹ If our proposals are correct then the basic structures of **1(C)** and **5 (E)** are fundamentally different.

The ^1H NMR spectrum of **5** shows no obvious neopentylidene H_α resonance, while the spectrum of **6** shows an H_α resonance at 4.09 ppm. We suspect that the α proton resonance in the spectrum of **5** occurs at slightly higher fields than it does in **4** and therefore is obscured by some nearby resonances for the TIPT ligand. ^{13}C NMR spectra show a resonance for the neopentylidene α carbon atom at 251.9 ppm with $J_{\text{CH}} = 76$ Hz in **5** (in THF-d_8) and at 252.4 ppm with $J_{\text{CH}} = 94$ Hz in **6** (in C_6D_6). The low value for J_{CH} and relatively high field chemical shift for H_α suggest that the alkylidene ligand probably is more distorted in **5** and **6** than it is in **1** and **2**. Since early studies showed that neopentylidene ligands are more distorted in iodide complexes than in bromide complexes, and more in bromide complexes than in chloride complexes,²⁰ one might expect the neopentylidene ligand in thiolate complexes to be more distorted than in analogous phenoxide complexes.

Both the phenoxide and the thiolate neopentylidene complexes react readily with the carbonyl functionality (1-2 eq in ether or a hydrocarbon at ~ 20 mM in Ta). **1** reacts with acetone rapidly at 25° to give 2,4,4-trimethyl-2-pentene; after 1 h the gc yield was found to be 95% of theory. The reaction between **1** and benzaldehyde gave a 96% gc yield of a 1.9:1 mixture of *trans*:*cis* Wittig products in 4 h at 40° . Benzophenone reacts with **1** more slowly (8 h at 40° , 88% yield by NMR) and *N,N*-dimethylformamide slower still (10 h at 40° , 95% yield by NMR, all *trans*). The tantalum product in all cases is a white powder that is insoluble in common solvents. We believe it must be $[\text{Ta}(\text{O})(\text{DIPP})_3]_x$ in which bridging oxo ligands form the backbone of the polymer chain. The reaction between **5** and benzaldehyde at 25° gives the expected Wittig products (1.0:1.0 *trans*:*cis* ratio) in 82% yield after 25 minutes. We presume the tantalum product is an oxo complex; under these conditions it was an orange oil and was not characterized. These Wittig-like reactions are analogous to those observed in studies involving $\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_3$.^{12a}

Reactions of DIPP Complexes with Acyclic Olefins

$\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ reacts rapidly with one equivalent of styrene to give a molecule whose ^1H and ^{13}C NMR spectra suggest that it is a tantalacyclobutane complex that contains one α

and one β substituent (7). The α proton resonances are found at 3.10-2.85 (area 2) and 2.17 ppm (area 1), and the β proton resonance at 1.57 ppm (Table II). The α carbon resonances are found at 81.9 ppm ($J_{CH} = 133$ Hz) and 63.8 ppm ($J_{CH} = 129$ Hz), and the β carbon resonance is found at 42.9 ppm ($J_{CH} = 125$ Hz). In C_6D_6 at 25° all DIPP ligands appear to be equivalent, although the DIPP methyl groups are diastereotopic. These results are those to be expected for either $Ta[CH(^tBu)CH(Ph)CH_2](DIPP)_3$ or the less logical $Ta[CH(Ph)CH(^tBu)CH_2](DIPP)_3$. In either molecule a fluxional process must readily interconvert the DIPP ligands, but no plane of symmetry can be generated in the process.

An X-ray study showed that 7 is actually the less logical of the two possibilities (i.e. $Ta[CH(Ph)CH(^tBu)CH_2](DIPP)_3$). The structure is of poor quality, so we cannot place too much emphasis on detailed comparisons. Bond distances and angles are listed in Table III, and a drawing of one of the two crystallographically independent molecules is provided as Figure 1. One can argue that 7 is best described as a distorted square pyramid with O(21) at the apex. The largest interligand angle is C(43)-Ta-O(11) ($150.9(8)^\circ$) followed by C(41)-Ta-O(31) ($128.8(7)^\circ$) and O(21)-Ta-O(31) ($120.2(7)^\circ$). If O(21)-Ta-O(31) were between 100° and 110° then the structure would be close to an ideal square pyramid. This ill-defined geometry contrasts with the fairly rigorous trigonal bipyramidal geometry found in $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ ($NAr = N-2,6-C_6H_3^iPr_2$),^{2b,21a} $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$,^{21a} and closely related $Ta[CH(C_5H_8)CHCH(^tBu)](DIPP)_3$ (see later) where the MC_3 ring occupies equatorial coordination sites. Square pyramidal structures are found occasionally in tantalum(V) chemistry.^{21b,c} The reason why the structure of 7 is relatively far from an ideal is unclear at this point. It is interesting to speculate, however, that 7 might more readily lose an olefin than an analogous TBP complex, and since these molecules are so fluxional, that intermolecular packing forces may dictate the structure. Since we now know that square pyramidal tungstenacyclobutane complexes are sometimes the most stable form^{21d} (one has been characterized structurally), a square pyramidal structure for a metallacyclobutane complex perhaps should always be considered

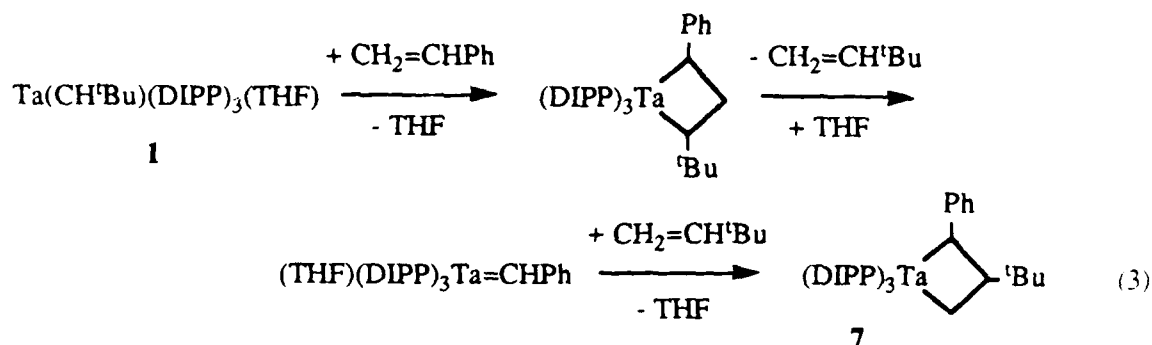
as a distinct alternative to a trigonal bipyramidal structure in metathetical reactions. We will come back to some of these points later.

The Ta-O and Ta-C bond lengths in the structure of **7** are not unusual, although the shortest Ta-O distance (1.820(14) Å) is marginally shorter than the Ta-O distance (1.836(4) Å) reported by Rothwell for Ta(O-2,6-C₆H₃^tBu)₂Cl₃ and said to be the shortest Ta(V)-aryloxide bond to date.^{21c} The Ta-O-C angles also are not unusual, the range being 146.3(15) to 157.0(13)°, characteristic of alkoxides bound to relatively electron-deficient early transition metals.²² The Ta-C bond lengths are at the lower end of the range for Ta-C single bonds (2.15 - 2.25 Å).

The TaC₃ ring is slightly bent with the α (phenyl) and β (t-butyl) substituents *trans* to one another. The dihedral angle between the C(41)/C(42)/C(43) and Ta/C(41)/C(43) planes of 25.2° places the α and β substituents in pseudoequatorial positions.²³ The long C-C bonds within the TaC₃ ring also are characteristic of (all carbon) metallacycles of d⁰ metals,^{24b,d} although the large esd's in this particular case prevent our knowing whether these bond lengths fall in the upper or lower end of the range. One potentially important feature of this MC₃ ring system relative to those found in TBP complexes is that it is elongated in the Ta...C_β direction, i.e., C(41)-Ta-C(43) = 64.4(9)°, Ta-C(41)-C(42) = 94.2(14)°, Ta-C(43)-C(42) = 97.0(15)°, C(41)-C(42)-C(43) = 98.4(18)°, and Ta...C(42) = 2.782(24) Å. These values are compared in Figure 2 with those found in the TaC₃ ring in Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃ (see later) and the WC₃ ring in W[CH(SiMe₃)CH(SiMe₃)CH₂](NAr)[OCMe(CF₃)₂]₂.^{2b,21a} We ascribe this elongated ring shape to the fact that **7** is *not* a trigonal bipyramidal species; a smaller C_α-Ta-C_α angle and longer Ta...C_β distance would be expected if the ring carbons occupy basal positions in a square pyramid than if they occupy equatorial positions in a trigonal bipyramid.

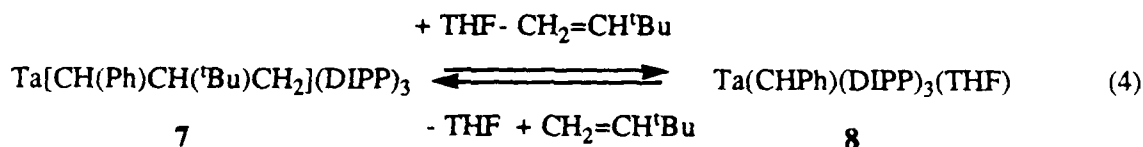
Most likely the initial tantalacycle that forms when **1** reacts with styrene loses t-butylethylene, which then adds back to the incipient benzyldiene complex to give **7** (equation 3). If we ignore electronic factors then we might predict this result on steric grounds alone, assuming that formation of a tantalacycle is readily reversible in the presence of THF, i.e. the two ring

substituents should be located in pseudo-equatorial positions as far from the bulky alkoxide ligands



as possible (on α and β carbon atoms), and the more bulky of the two should reside on the β carbon atom.^{24a}

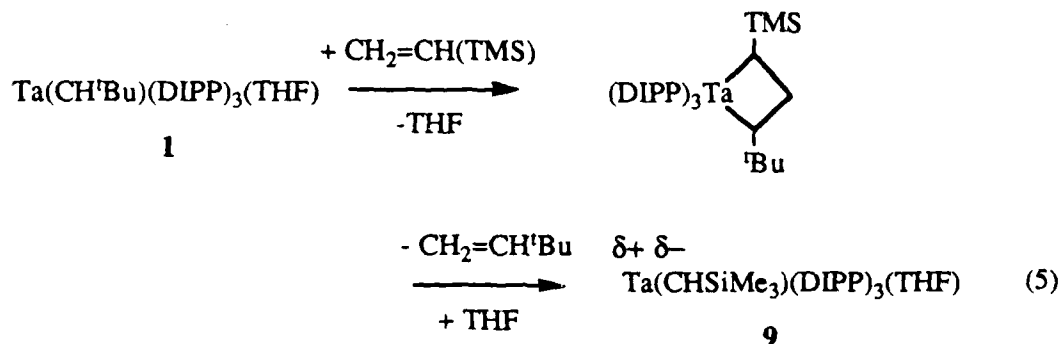
The addition of THF to **7** yields $\text{Ta}(\text{CHPh})(\text{DIPP})_3(\text{THF})$ (**8**) and t-butylethylene, reversibly (equation 4). In a typical reaction **7** and **8** are in equilibrium in C_6D_6 in the presence of



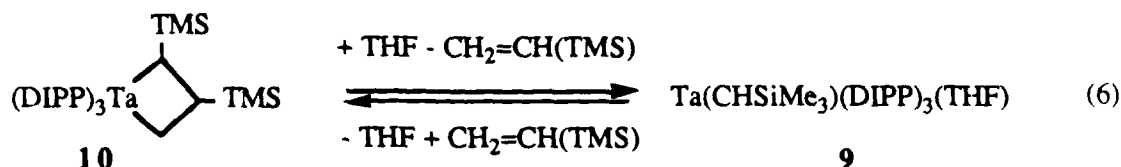
several equivalents of THF. $\text{Ta}(\text{CHPh})(\text{DIPP})_3(\text{THF})$ can be isolated by treating **1** with styrene in the presence of a large excess of THF, followed by removal of t-butylethylene *in vacuo*. The chemical shift of H_α in **8** (8.49 ppm) is substantially greater than that in **1** (5.73 ppm) and J_{CH} (114 Hz) is the largest of any molecule of this type (Table I).

$\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ reacts with one equivalent of vinyltrimethylsilane to give $\text{Ta}(\text{CHSiMe}_3)(\text{DIPP})_3(\text{THF})$ (**9**) in high yield (equation 5). The formation of **9** is significantly *accelerated* when the reaction is performed in the presence of excess THF. We postulate that vinyltrimethylsilane in effect displaces THF from $\text{Ta}(\text{CHR})(\text{DIPP})_3(\text{THF})$ and that olefin is ejected from the intermediate tantalacycle when it is attacked by THF (equation 5). It is not unexpected to

find that **9** is favored over **1**, a result that would be consistent with the well-known ability of silicon to stabilize an adjacent negative charge on the alkylidene α carbon atom.



When **9** is treated with one or more additional equivalents of vinyltrimethylsilane, or when **1** is treated with several equivalents of vinyltrimethylsilane over a period of several hours, colorless $\text{Ta}[\text{CH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{CH}_2](\text{DIPP})_3$ (**10**) can be isolated in good yield. Addition of THF to **10** yields solutions that contain both **9** and **10**, suggesting that the equilibrium shown in equation 6 is readily attained. (An ^1H NMR spectrum of a C_6D_6 solution containing **10** (~50 mM) and 4 eq of THF showed a mixture of 84% **10** to 16% **9** at 25°, and 73% **10** to 27% **9** at 50°.)

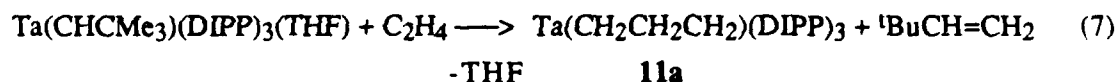


^1H and ^{13}C NMR data suggest that the substituents in **10** are located on α and β ring carbon atoms (Table II), probably mutually *trans* to one another, as found in $\text{W}[\text{CH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{CH}_2](\text{N}-2,6-\text{C}_6\text{H}_3\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$.^{2b,21a} The ^1H NMR spectrum of **10** displays broad resonances for the DIPP ligands, but the ring protons give rise to relatively sharp signals at 4.98 (t, 1), 3.64 (t, 1), 2.95 (d, 1), and -0.33 (m, 1). A ^{13}C NMR spectrum displayed resonances for the ring carbons at 108.1 (t, C_α), 99.3 (d, C_α), and 6.41 (d, C_β) ppm. ^1H NMR decoupling experiments provided further support for an α , β substituted ring. The 4.98

and 3.64 ppm resonances can be ascribed to inequivalent α methylene protons, the -0.33 ppm resonance to β CH(TMS), and the 2.95 ppm resonance to α CH(TMS).

Close examination of NMR spectra of **10** suggests that a small amount of the α,α substituted isomer (~15%) may be present. (A ^1H NMR multiplet at 3.93 ppm can be assigned to α CHSiMe₃ and a ^{13}C NMR doublet at 106.2 ppm ($J_{\text{CH}} = 122$ Hz) to α CHSiMe₃.) In the related tungsten complex, W[CH(SiMe₃)CH(SiMe₃)CH₂](N-2,6-C₆H₃ⁱPr₂)[OCMe(CF₃)₂]₂,^{2b,21a} only the α,β isomer is observed, and on the basis of a crystal structure it could be argued that the α,α isomer should be unfavorable for steric reasons in that case. The DIPP ligands in **10**, however, could be more tolerant of the sterically demanding α,α disubstitution since the molecule is not stereochemically rigid and may not be rigorously trigonal bipyramidal.

Ta(CHCMe₃)(DIPP)₃(THF) reacts virtually instantaneously with 30 psi of ethylene to give colorless Ta(CH₂CH₂CH₂)(DIPP)₃ (**11a**) and 0.90 equivalents of *t*-butylethylene (equation 7). Ta[CH(^{*t*}Bu)CH₂CH₂](DIPP)₃, the presumed intermediate in this reaction, has never been



observed under these conditions. In the ^1H NMR spectrum of **11a** (in C₆D₆) the α proton resonance consists of a doublet of doublets at 3.86 ppm, and the β proton resonance as a multiplet at 0.48 ppm. A ^{13}C NMR spectrum shows a resonance for the α ring carbon atom at 96.1 ppm ($J_{\text{CH}} = 147$ Hz) and for the β ring carbon atom at -0.68 ppm ($J_{\text{CH}} = 150$ Hz). In both ^1H and ^{13}C NMR spectra, only a single set of DIPP ligand resonances is observed at 25°.

THF does not react readily with **11a**, although pyridine does react readily with **11a** to give what appears to be an unstable adduct, Ta(CH₂CH₂CH₂)(DIPP)₃(py) (**11b**). **11b** is the only example of a base adduct of a tantalacyclobutane complex that we have observed. Similar adducts may be intermediates in reactions of various other tantalacycles with donor ligands, or in reactions of alkylidene complexes with olefins, although it is impossible to predict how stable such intermediates might be, and therefore whether they should be included as part of a mechanism.

Substitution of the TaC₃ ring is likely to significantly increase steric crowding about the metal, perhaps to the extent that a six-coordinate THF adduct would have virtually no stability.

The NMR data for **11b** need to be looked at closely, since we now have good reason to believe that ¹H and ¹³C NMR chemical shifts (and probably also CH coupling constants) are sensitive to the overall structure of the metallacyclobutane complex, and in particular to the detailed structure of the metallacyclic ring, i.e., whether the metal...C_β distance is "long" (as in **7**) or "short" (as in trigonal bipyramidal metallacyclobutane complexes). A ¹H NMR spectrum of **11b** at 25° (C₆D₆) displays resonances for the α protons at 2.95 ppm and the β protons at 2.00 ppm. Since only one set of resonances is observed when free pyridine is added to the sample we believe that pyridine is lost readily from **11b** to give **11a**. Upon heating a sample of **11b** the α proton resonance shifts downfield and the β proton resonance shifts upfield, further suggesting that **11b** is in equilibrium with **11a** and pyridine. Unfortunately, spectra at low temperatures were too complex to allow us to conclude whether **11b** is a single isomer or not, and if it is a single isomer, what its structure might be. Nevertheless, the fact that the average α and average β proton resonances in **11b** are not as disparate as they are in **11a** we believe is consistent with a now higher coordinate metallacycle in which the metal...C_β distance is significantly longer and C_α-M-C_α angle is significantly smaller than it is in five-coordinate, trigonal bipyramidal species. Analogous trends are observed in the ¹³C NMR spectra of **11b**. The α carbon resonance is found at 78.0 ppm (*J*_{CH} = 120 Hz) and the β carbon resonance at 36.3 ppm (*J*_{CH} = 129 Hz), in sharp contrast to what is found for **11a** (96.1 and -0.68 ppm, respectively; Table II). Neither **11a** nor **11b** is stable in solution over an extended period of time. They (especially **11b**) slowly decompose to give dark solutions in which no product has yet been identified. In one instance in the process of collecting ¹³C NMR data on **11b** we observed a triplet resonance at 217.4 ppm with *J*_{CH} = 135 Hz that almost certainly can be ascribed to a methylene complex, perhaps Ta(CH₂)(DIPP)₃(py)₂ (cf. δ C_α = 252.2 ppm with *J*_{CH} = 145 Hz in W(CH₂)(N-2,6-C₆H₃iPr₂)[OCMe(CF₃)₂]₂(PMe₃)^{21a}). However, this species also decomposed readily, and no attempt was made to isolate it.

$\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ reacts rapidly with propylene or 1-butene to give nearly colorless solutions initially. However these solutions begin to darken rapidly upon work-up. We have tried to identify products *in situ*, but so far without success. We believe that tantalacyclobutane complexes form, but alkylidene complexes of the type $\text{Ta}(\text{CHR})(\text{DIPP})_3(\text{THF})$ in which the alkylidene ligand contains β hydrogen atoms probably are unstable. Addition of excess *cis*-2-pentene to **1** in ether or a hydrocarbon results in a lightening of the solution and rapid metathesis (100 eq to equilibrium in < 15 m). However, addition of a second aliquot of *cis*-2-pentene showed that the catalyst was no longer active, further evidence that intermediate alkylidene complexes are unstable. These findings are analogous to those in earlier systems employing phosphine-substituted niobium and tantalum complexes.¹⁰ It is also possible that intermediate tantalacyclobutane rings rearrange to olefins,¹⁰ although we think this a less likely possibility in view of what appears to be the relatively high stability of the tantalacyclobutane complexes that we have isolated so far. The activity of the $\text{Ta}(\text{CHR})(\text{DIPP})_3(\text{THF})$ system qualitatively is significantly greater than the activity of the phosphine-substituted catalysts.¹⁰ One possible explanation is that $\text{Ta}(\text{CHR})(\text{DIPP})_3(\text{THF})$ complexes actually *are* more stable toward rearrangement to an olefin than tantalum alkylidene complexes that contain phosphine ligands.

$\text{Ta}(\text{CH}^t\text{Bu})(\text{DMP})_3(\text{THF})$ does not react cleanly with ethylene. No products could be isolated, and a ^1H NMR spectrum of the crude reaction mixture showed many unidentifiable resonances. We speculate that DMP ligands probably are small enough to behave as donors in intermolecular reactions that result in loss of ethylene and subsequent decomposition of the incipient methylene complex.

Reactions of TIPT Complexes with Acyclic Olefins

The TIPT complex **5** does not react with ordinary olefins (e.g. *cis*-3-hexene) over a period of several hours at 25°. Likewise, **5** does not metathesize 2-pentenes at 25° or 50°. A similar lack of reactivity (relative to the corresponding phenoxide species) has been documented for some benzenethiolate alkylidyne complexes of molybdenum and tungsten.¹⁹ The reasons why **5** is relatively unreactive toward ordinary olefins may not be straightforward (see DISCUSSION).

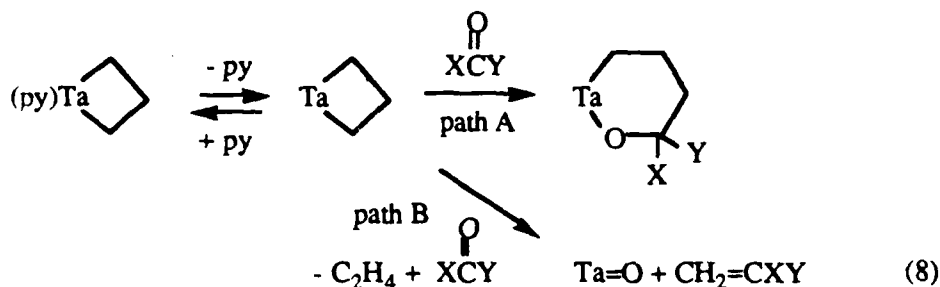
Lack of reactivity of TIPT complexes with acyclic olefins is a disadvantage to the extent that it prevents us from preparing other types of alkylidene complexes from 5. However, this lack of reactivity can be turned into an asset, as we shall see later when we discuss reactions of neopentylidene complexes with norbornene.

Reactions of Metallacycles with the Carbonyl Functionality

Since tantalacyclobutane complexes react with THF or pyridine to give alkylidene complexes, we thought that they probably would react with organic compounds that contain the carbonyl functionality to give Wittig products via an incipient tantalum alkylidene complex.¹² This turns out to be the case, but the situation is complicated by direct reaction of the carbonyl compound with the tantalacycle to give oxytantalacyclohexane complexes via insertion of the organic carbonyl into a tantalum-carbon bond. In this section we discuss various examples of reactions of tantalacycles with carbonyl compounds. We have not explored this subject deeply since at this stage we are interested primarily in determining trends, and in particular, in determining what carbonyl compound yields Wittig products most efficiently.

Upon exploring reactions involving 11a and 11b (Table IV) we noticed that they react similarly with ketones and aldehydes, a result that suggests that the reactive species is the base-free tantalacycle (equation 8; DIPP ligands omitted). Reaction of the base-free tantalacycle with the carbonyl compound via path A then competes with loss of ethylene and reaction of the incipient methylene complex (path B). We must consider the possibility that path B also proceeds under some circumstances via a carbonyl adduct of the tantalacycle, i.e., loss of ethylene is promoted by coordination of the carbonyl. For benzophenone the reaction follows mostly path B, while for acetone, benzaldehyde, or pivaldehyde the reaction proceeds primarily via path A. Most tantalacyclohexane insertion products (the exception being that formed from benzophenone) are quite stable thermally, showing little, if any, decomposition after being heated overnight in C₆D₆ at 70°. We are assuming that the insertion reaction proceeds so as to place the oxygen in the ring next to the metal, and that the carbonyl carbon atom is still bound to that oxygen. Related insertion reactions have been reported previously,^{24c,e,f,25} and one X-ray study²⁵ shows that the oxygen is

bound to zirconium. Proton and carbon NMR data for oxyantalacyclohexane complexes can be found in the Experimental Section.

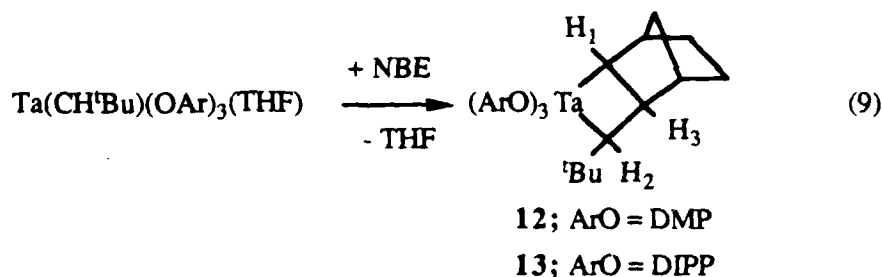


The second trend that we have observed for reactions involving **11a** and **11b** is that at higher temperatures more Wittig products are observed (Table IV), consistent with a greater entropic contribution to the temperature dependence of the rate constant for path B.

Third, one might predict that an olefin is lost more readily from a more crowded disubstituted tantalacycle, and that therefore little or no insertion chemistry of such tantalacycles should be observed. Indeed, **7** reacts with acetone at 25° to give ~90% Wittig products, with no sign of any insertion reaction. We will show later that a trisubstituted tantalacycle reacts even with benzaldehyde to give only the Wittig product.

Isolable Tantalacyclobutane Complexes Prepared by Reaction of Ta(CH^tBu)(OAr)₃(THF) (OAr = DIPP or DMP) with Norbornene

Addition of 1 eq of norbornene at -30° to **3** in ether produces a yellow solution from which a yellow oil is obtained by removing all solvent *in vacuo*. Very pale yellow microcrystals that are extremely soluble in pentane can be obtained in 31% yield from concentrated solutions at -30°. The NMR spectra of the oil and the crystals are identical except for minor impurity peaks in the former. A ¹H NMR spectrum of the crystals is shown in Figure 3. It is consistent with the product being the tantalacyclobutane complex **12** (equation 9; ring stereochemistry unknown).



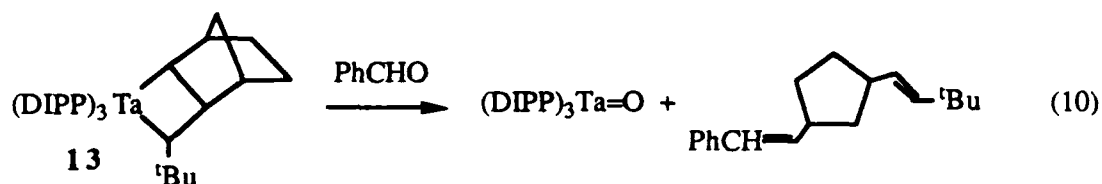
The most characteristic features of the spectrum are the resonances at 5.21(d), 3.72(d), and 0.84(t), assignable to protons H₁, H₂, and H₃, respectively. (The H₁ and H₂ resonances can be distinguished on the basis of the reaction of 13 with norbornene-2,3-d₂; see later.) In a similar titanacyclobutane complex, Cp₂Ti[CH(R)CH(C₅H₈)CH] (R = Me₂CCH=CH₂), these signals are found at 3.72, 2.63, and 0.08 ppm.^{13a} The ¹³C NMR spectrum of 12 shows signals for all 15 carbon atoms, the tantalacycle ring carbon resonances being observed at 132.5, 135.0, and 29.0 or 30.2 (Table II; cf. 110.9, 104.4, and 24.2 ppm in Cp₂Ti[CH(R)CH(C₅H₈)CH]^{13a}).

An analogous reaction between 1 and norbornene yields more crystalline, colorless 13 in 64% isolated yield (recrystallized from ether). NMR spectra of 13 are analogous to those of 12 as far as the TaC₃ ring is concerned (Table II). However, the DIPP resonances are broad, characteristic of an intermediate rate of a fluxional process in a tantalacyclobutane complex in which they are not all equivalent. 13 is stable as a solid at 25°, but decomposes to the extent of 10-20% after one day in C₆D₆.

An X-ray structure study showed 13 to have a geometry close to trigonal bipyramidal (Figure 4; Table V) with O-Ta-O angles of only slightly less than 90° or 180°. All of the Ta-O bond lengths are similar (~1.91 Å; Table V) as are all Ta-O-C angles (159-164°). All values are within the range of metal-oxygen and metal-O-C angles that are normally observed for early transition metal phenoxide complexes.²² The two ring α carbon atoms lie essentially in the equatorial plane with C_α-O_{ax} bond angles of near 90° and C_α-O_{eq} bond angles of 136.1(5)° and 145.1(6)°.

The tantalacyclic ring system in **13** is remarkably similar to the tungstacyclic ring system in $W[CH(SiMe_3)CH(SiMe_3)CH_2](N-2,6-C_6H_3^iPr_2)[OCMe(CF_3)_2]_2$ (Figure 2).^{21a} The main difference between the ring system in **13** and that in **7** is that the ring in **7** is much more elongated (as we mentioned earlier); the Ta...C β bond distance in **7** is 2.782(24) Å, while it is 2.382(16) Å in **13**. We assume, therefore, that the ring systems in $W[CH(SiMe_3)CH(SiMe_3)CH_2](N-2,6-C_6H_3^iPr_2)[OCMe(CF_3)_2]_2$ and **13** are characteristic of complexes in which the overall structure is close to trigonal bipyramidal. There are three other tungstacyclobutane complexes that have been structurally elucidated; two are trigonal bipyramids and have ring systems closely analogous to that found in **13**,^{21a} and the third is a square pyramid with a ring closely analogous to that found in **7**.^{21d} The ring in **13** is bent less ($\sim 15.5^\circ$) than the ring in **7**, perhaps in part because the geometry about the C(42)-C(43) bond is necessarily *cis*.

The trisubstituted tantalacycle **13** reacts with benzaldehyde to give the expected Wittig products, as shown in equation 10 (reaction with 3 eq of benzaldehyde is complete within ~ 30

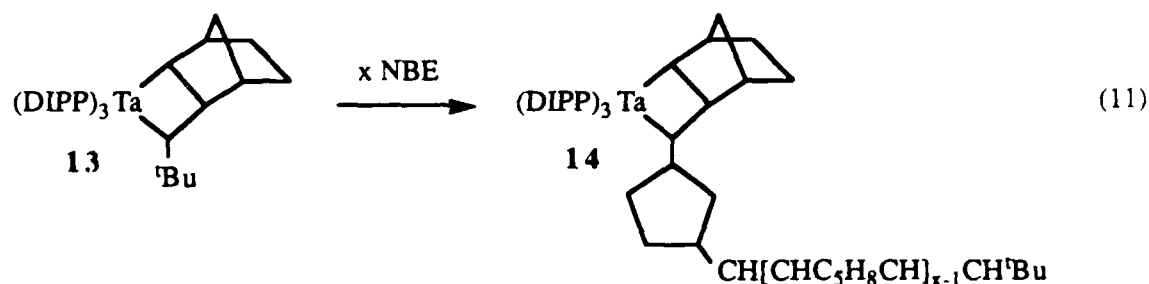


minutes at 50° in C_6D_6 at a concentration of **13** of ~ 50 mM). The observed pattern for the olefinic proton resonance on the phenyl-substituted end is consistent with a 2.7/1.0 *trans/cis* mixture of isomers, based on spin simulation experiments performed with the analogous complex **14** (see below). We cannot tell what the double bond geometry is at the other end by NMR; we presume it is all *trans* since the *t*-butyl group is *trans* to the norbornene ring in **13**.

Polymerization of Norbornene by DIPP Complexes

When **13** is heated with excess NBE in C_6D_6 , resonances characteristic of polynorbornene ($\sim 55\%$ *trans*) are observed, and resonances for the tantalacycle **14** appear (H_1 at 5.22 and H_2 at

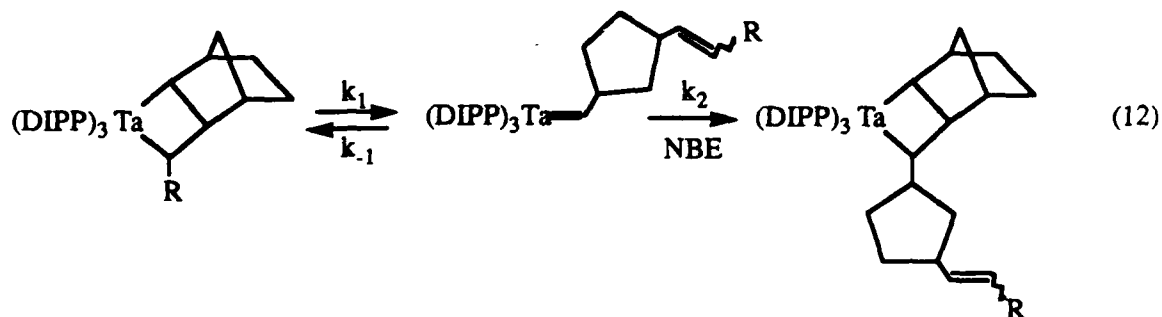
3.85 ppm) as those for **13** disappear (equation 11; it should be understood that there is the normal distribution of chain lengths about $x-1$). The reaction can be taken to completion (Figure 5) with no sign of degradation of the catalyst. The polymerization can be stopped by cooling the reaction mixture (from 50° to 25°). After reheating it to 50° the polymerization



resumes at the same rate as before. In the absence of NBE **14** decomposes to the extent of ~5 to ~10% after 24 hours at 25°, but in the presence of NBE it does not decompose to any extent observable by NMR (< 5%) in the same time period. In the absence of NBE the *cis* double bonds in the polymer isomerize slowly. For example, in reactions in which $x = 10-20$ the *trans* content increases from 55% to ~65% in five days in C_6D_6 . We assume that isomerization results from metathesis reactions and that either some decomposition product or the alkylidene formed by ring-opening of **14** is the catalyst. (As we shall show later the polydispersity of the polynorbornene increases with time, characteristic of metathesis reactions involving the double bonds in the polymer chain.) Polynorbornene is readily cleaved from the metal center in **14** by treatment with carbonyl compounds, preferably benzaldehyde. Addition of 3 eq of benzaldehyde to **14** at 65° in C_6D_6 results in essentially quantitative formation of $\text{PhCH}(\text{CHC}_5\text{H}_8\text{CH})_{x+1}\text{CH}^t\text{Bu}$ within 20 minutes. The stereochemistry at the site of cleavage (i.e., in the phenyl-substituted double bond) is 68% *trans* and 32% *cis*, based on spin simulation studies (Figure 6; details in Experimental Section).

It is relatively simple to prepare samples of polynorbornene employing 13 as the catalyst in toluene in the presence of norbornene. The reaction is heated and the consumption of NBE is monitored. After polymerization is complete 20-30 eq of benzaldehyde are added, $[\text{Ta}(\text{O})(\text{DIPP})_3]_x$ is filtered off, and the resulting polymer analyzed by gel permeation chromatography. The results are summarized in Table VI; a representative GPC trace is displayed in Figure 9b. The molecular weight of the polynorbornene increases linearly with the number of equivalents of monomer, as expected for a living catalyst system. The higher than desired polydispersities (e.g., for 100 eq NBE, $M_n = 22,000$ and $d = 1.63$) can be ascribed to slow secondary metathesis reactions after all norbornene has been consumed. When a sample was heated for several hours after all of the monomer had been consumed, a polydispersity of 1.95 was observed (run 5). In one case (run 4) the polymerization was stopped at ~75% completion, and the polydispersity in that case (1.04) was what one would expect for a well-behaved living polymerization. Polydispersities increase as a result of metathesis (and accompanying isomerization) reactions after all NBE is consumed.

Kinetic studies demonstrated that the rate limiting step in this reaction is ring-opening of the metallacycle followed by a rapid reaction of the incipient alkylidene with NBE (equations 12 and 13). Kinetic data are listed in Table VII. A typical plot is shown in Figure 7. In the beginning of a typical run the rate of consumption of NBE is slightly less than the maximum value and increases



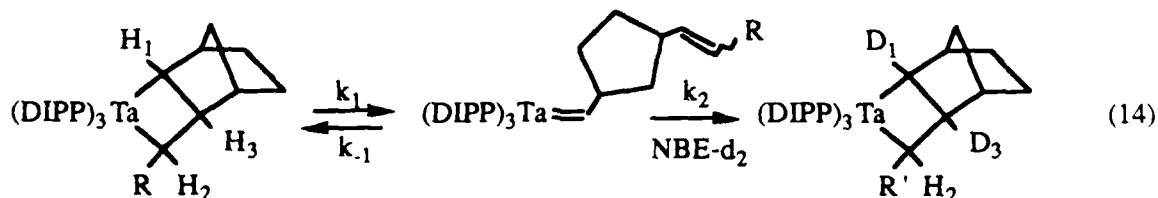
$$-\frac{d[\text{NBE}]}{dt} = \frac{k_1 k_2 [\text{Ta}][\text{NBE}]}{k_{-1} + k_2 [\text{NBE}]} \quad (13)$$

to that value after ~5 eq of NBE have been consumed, consistent with a slightly slower initial step (when R = t-butyl) relative to that when R is the growing polymer chain. The zero order dependence on [NBE] ($k_2[\text{NBE}] \gg k_{-1}$) continues throughout the reaction until 1 to 2 eq of NBE remain. Thereafter $k_2[\text{NBE}] \ll k_{-1}$. At 57° a $\ln[\text{NBE}]$ plot begun when ~1 eq of NBE remained yielded $k_2/k_{-1} \approx 150 \text{ M}^{-1}$ (estimated error $\pm 50 \text{ M}^{-1}$).

The rate of consumption of **13** was monitored at 35.0° by following the disappearance of the proton signal ascribed to H₂ at 3.88 ppm. A plot of $\ln[\text{13}]$ versus time yielded $k_1 = 3.9 \times 10^{-4} \text{ s}^{-1}$. The maximum rate of consumption of NBE (by **14**) at 35.2° was found to be $6.3 \times 10^{-4} \text{ s}^{-1}$. Therefore the rate of chain growth is approximately 50% faster than the rate of chain initiation. A detailed explanation is not possible since two propagating tantalacycles are involved, one in which the growing chain is *trans* to the C₅H₈ ring (as the t-butyl group is in **13**, i.e., **14_{trans}**), and another "all *cis*" tantalacycle (**14_{cis}**). We assume that **14_{trans}** gives rise to the *trans* C=C bond in the polymer, and **14_{cis}** to the *cis* C=C bond in the polymer, i.e., $k_1(\text{obs})[\text{Ta}_{\text{total}}] = k_1(\text{14}_{\text{trans}})[\text{Ta}_{\text{trans}}] + k_1(\text{14}_{\text{cis}})[\text{Ta}_{\text{cis}}]$. We would expect k_1 for **13** ($k_1(\text{13})$) to be greater than $k_1(\text{14}_{\text{trans}})$ since the t-butyl group in **13** for steric reasons should speed up opening of the ring. We propose that the difference between $k_1(\text{13})$ and $k_1(\text{14}_{\text{trans}})$ is more than negated by a relatively large value for $k_1(\text{14}_{\text{cis}})$, so that propagation ultimately is faster than initiation. Fortunately, the difference in the rate of propagation versus initiation has a negligible effect on the dispersity of polynorbornenes prepared in this manner.

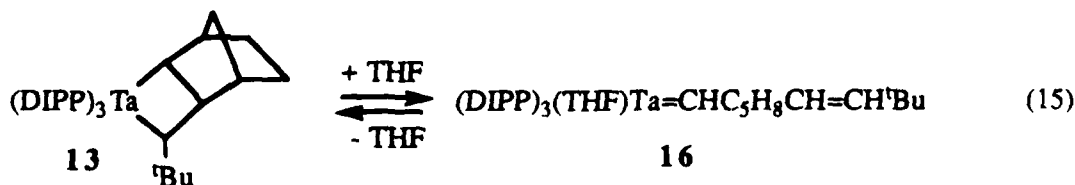
It is possible (but difficult) to isolate the "second insertion product," $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(\text{C}_5\text{H}_8\text{CH}=\text{CH}^t\text{Bu})](\text{DIPP})_3$ (**15**), by treating **13** with one equivalent of NBE followed by heating the mixture to 60°. A sample of **15** could be isolated as an *extremely* soluble white powder from concentrated pentane solutions. The ¹H NMR spectrum of **15** at 25° displays broad resonances for the DIPP ligands but relatively sharp signals for the α protons of the ring (H₁ at 5.23 ppm (d), H₂ at 3.85 ppm (~t)), about the same chemical shifts as the resonances for H₁ and H₂ in the spectrum of **14**; the β proton resonance in the spectrum of **15** is obstructed by other upfield resonances. The rate of ring-opening of **15** can be determined by monitoring the

disappearance of the H_1 resonance at 5.23 ppm (H_1) upon treating **15** with NBE-2,3- d_2 . The H_1 resonance was chosen because it is replaced by deuterium upon reaction with one equivalent of NBE-2,3- d_2 (equation 14), while conversion of H_2 to deuterium requires two equivalents



of NBE-2,3- d_2 . A plot of $\ln[15]$ versus time at 35.0° gave $k_1(15) = 9.8 \times 10^{-4} \text{ s}^{-1}$ (cf. $k_1(13) = 3.9 \times 10^{-4} \text{ s}^{-1}$ at 35.0° and $k_1(14) = 6.3 \times 10^{-4} \text{ s}^{-1}$ for consumption of NBE at 35.2° by **14**_{cis} plus **14**_{trans}). The only way we can explain the large value for $k_1(15)$ relative to $k_1(14)$ (the observed rate for NBE bulk polymerization) is to assume that isolated **15** is *not representative* of the mixture of *cis* plus *trans* tantalacycles in solution, i.e., it contains a significantly higher percentage of the *cis* tantalacycle, the rate of opening of which must be faster than the rate of opening of the *trans* tantalacycle, as noted above.

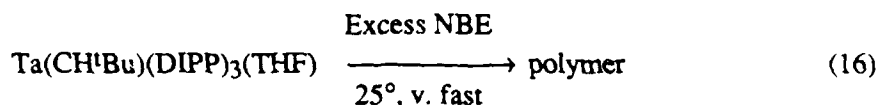
Upon heating a solution of **13** in THF- d_8 at 65° signals characteristic of an alkylidene complex ($\delta H_\alpha = 7.69$ ppm, $J_{HH} = 8.6$ Hz; $\delta H_\beta = 4.54$ ppm (m)) grow in slowly. We propose that this alkylidene complex is **16** (equation 15), and that it is formed by rate limiting ring-opening of **13** followed by trapping of the incipient alkylidene by THF. The consumption of NBE at elevated temperatures in the presence of 5-10 eq of THF is the same as in the absence of THF,



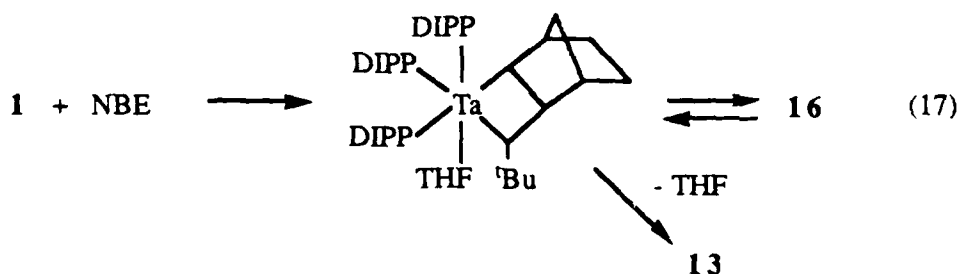
a fact that suggests that ring-opening *in this case* (see earlier examples to the contrary) is rate

limiting and that NBE is a significantly better trap for the incipient alkylidene complex than THF is. In solvents other than THF (ether, pentane, C₆D₆) **16** loses THF and **13** reforms.

There is one last observation that deserves some comment. Addition of excess NBE to **1** at 25° leads to rapid formation of polynorbornene and complete consumption of **1** (equation 16), even in neat THF. We speculate that an initial six-coordinate tantalacycle forms that is in equilibrium



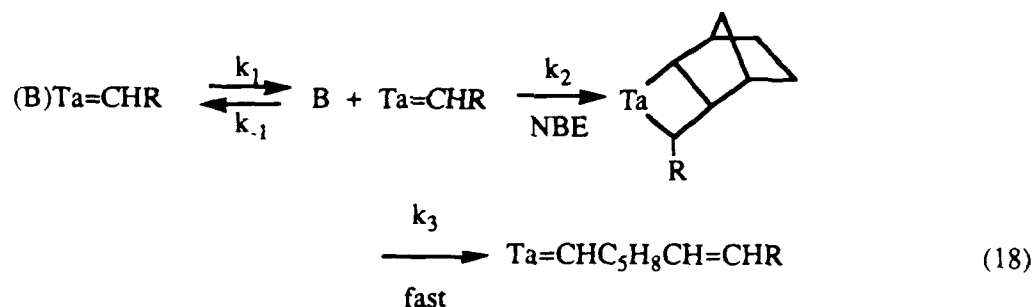
with **16** and that *relatively* slowly loses THF to give **13** (equation 17). If excess NBE is present then **16** reacts rapidly to give another six-coordinate tantalacycle that ring-opens readily,



etc., i.e., a kinetically distinct "base-on" mechanism can be operative. Once "base-free" five-coordinate tantalacycles form (**13** and **14**), then polymerization of norbornene proceeds via the mechanism involving rate-limiting ring-opening in these five-coordinate tantalacycles (a much slower process). GPC analysis of a polynorbornene polymer sample prepared by adding 200 equivalents of NBE to **1** in toluene (Table VI, run 11) supports this speculation. The polynorbornene has a high molecular weight and large polydispersity ($M_n = 146,000$; $d = 4.41$) along with a low molecular weight tail, features that could arise from a highly active polymerization catalyst that is deactivated over the course of the polymerization reaction by formation of **13** and **14**, species that are relatively inactive at room temperature.

Reactions of TIPT Complexes with Acyclic Olefins and NBE.

As mentioned previously, neither **5** nor **6** reacts with ordinary olefins such as *cis*-3-hexene or 2-pentenes. However, **5** does react rapidly with NBE at 25° in ether or toluene to give polynorbornene (~70% *cis*). When **5** was treated with 10 eq of NBE in ether, the ¹H NMR spectrum of the resulting product (in C₆D₆) showed only resonances consistent with the formation of Ta[(CHC₅H₈CH)_xCH^tBu](TIPT)₃(THF), none for **5**. The α proton resonance was not located in the spectrum of Ta[(CHC₅H₈CH)_xCH^tBu](TIPT)₃(THF); it was not in the spectrum of **5** either (see above). Neither **5** nor Ta[(CHC₅H₈CH)_xCH^tBu](TIPT)₃(THF) reacts with NBE at 25° in THF, a fact that suggests that activity probably depends on the accessibility of a base-free intermediate (i.e. Ta(CH^tBu)(TIPT)₃; equation 18, TIPT ligands omitted). At no time do we see ¹H NMR resonances characteristic of a tantalacyclobutane complex. Therefore we propose that k₃ is fast.



There is other evidence for the "base-free" mechanism. The pyridine adduct **6** does not react with NBE at 25° in toluene, pentane, or ether. At elevated temperatures where a base-free intermediate is present in much higher concentration, **6** does react with excess NBE to give polymer (~65% *cis*). In a typical spectrum, the α proton resonance for **6** disappears as new resonances for what we believe to be Ta[(CHC₅H₈CH)_xCH^tBu](TIPT)₃(py) appear (Figure 8); **6** is consumed completely by 5-6 eq of NBE. As in reactions involving **5** the alkylidene α proton resonances in Ta[(CHC₅H₈CH)_xCH^tBu](TIPT)₃(py) were not positively identified in the ¹H

NMR spectrum, but the alkylidene α carbon resonance can be seen at 249.3 ppm in the ^{13}C NMR spectrum of $\text{Ta}[(\text{CHC}_5\text{H}_8\text{CH})_x\text{CH}^t\text{Bu}](\text{TIPT})_3(\text{py})$ in C_6D_6 at 25° . As one would expect the rate of consumption of NBE at 50° in the presence of 3 eq of added pyridine ($[\text{6}] = 19 \text{ mM}$) was drastically reduced (by a factor of ~ 400 ; Table VII) compared to that in the absence of added pyridine.

According to the mechanism shown in equation 18 the rate of consumption of NBE should follow first order kinetics under any given set of conditions (equation 19). This was the case for the rate of disappearance of NBE in the presence of **6** in C_6D_6 at 39.8° ($k_{\text{obs}} = 4.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) and 49.0° ($k_{\text{obs}} = 8.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) (see also Table VII). The relatively small value of k_1/k_{-1} makes a detailed study of the rate versus $[\text{B}]$ impractical.

$$-\frac{d[\text{NBE}]}{dt} = \frac{k_1 k_2 [\text{Ta}][\text{NBE}]}{k_1 + k_{-1}[\text{B}]} \quad (19)$$

Reaction of $\text{Ta}[(\text{CHC}_5\text{H}_8\text{CH})_x\text{CH}^t\text{Bu}](\text{TIPT})_3(\text{THF})$ (or **6** at elevated temperatures) with 3 equivalents of benzaldehyde in C_6D_6 at 25° results in a complete cleavage of the polymer chain within 30 minutes. The configuration in the phenyl-capped double bond was found to be 64% *cis* on the basis of spin simulation studies (see Experimental Section for details). The results of GPC analysis of the benzyldiene-capped polynorbornene samples prepared using **5** and **6** are shown in Table VI. Consistent with a living polymerization system in which the rate of propagation is of the same magnitude as the rate of initiation, the molecular weights of the polynorbornene samples increase linearly with the number of monomer equivalents employed, and in all cases the polydispersities are representative of essentially monodisperse samples (a typical trace is shown in Figure 9a). In contrast to what was found with the DIPP catalysts, additional reaction time does *not* significantly affect polydispersity: 200 equivalents of NBE polymerized by **5** gave $M_n = 59,100$ ($d = 1.05$) after 20 minutes (the consumption was complete at this time) and $M_n = 57,600$ ($d = 1.07$) when a reaction was allowed to run for 55 minutes before quenching with

benzaldehyde. Therefore, the polymerization of NBE by **5** or **6** is well-behaved, yielding monodisperse polymers that are *not* subject to isomerization by the catalyst (cf. the DIPP system).

Polymerization of Norbornene by the DMP System.

The DMP tantalacyclobutane complex **12** reacts with NBE in a manner that in some respects is similar to the mode of reactivity observed for **13**. When **12** is heated with excess NBE in C_6D_6 new resonances indicative of the tantalacycle $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$ (P = polymer, 55% *trans*) are observed. **12** is consumed by 5 eq of NBE. However, the rate of consumption of NBE by **12** was found to be neither cleanly zero order nor first order in NBE in experiments in which $[12]_0 \approx 5$ mM and $[NBE]_0 = 50-75$ mM. For this reason we have not attempted to study the DMP catalyst system in any detail.

A NBE polymerization reaction catalyzed by **12** can be taken to completion and left at 50° with no sign of degradation of $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$. Solutions of $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$ in C_6D_6 in the absence of NBE show no *obvious* signs of decomposition even after several days at 25° , although the double bonds in the polymer isomerize to ~70% *trans* during this time ($x = 10-20$). Polymerization of 100 equivalents of NBE by **12** yields a polymer that by GPC analysis has $M_n = 10,700$ and $d = 2.71$ (Table VI). We could ascribe the high polydispersity to a greater metathesis activity toward double bonds in the polymer chain (after consumption of NBE), although mechanistic complications hinted at by the lack of well-behaved kinetics (see above) might also lead to broadening of the molecular weight distribution.

DISCUSSION

There are some results in the literature that correlate olefin metathesis activity with the electron withdrawing power of the alkoxide ligand. In complexes of the type $M(CHR')(NAr)(OR)_2$ ($M = Mo$ or W ; $Ar = 2,6-C_6H_3^iPr_2$), the activity of the catalysts for a given metal increases significantly in the series $OCMe_3 < OCMe_2(CF_3) < OCMe(CF_3)_2$.^{2,4,21a} Related observations had been made in acetylene metathesis reactions catalyzed by well-characterized alkylidyne complexes of the type $M(CR')(OR)_3$ ($M = Mo$ or W).¹ In both olefin and acetylene

metathesis systems intermediate metallacycles *in general* appear to be more stable toward loss of olefin (or acetylene) when electron-withdrawing alkoxide ligands are present. Finally, virtually no acetylene metathesis activity was observed for complexes of the type $M(CR')(SAr)_3$ ($M = Mo$ or W ; $Ar = 2,4,6-C_6H_2^iPr_3$ or $2,4,6-C_6H_2Me_3$).¹⁹ The trend that is appearing (at least for Mo and W) is that electron-withdrawing ligands in general (but not without exception even at this stage^{21a}) activate the metal toward reaction with a carbon-carbon multiple bond and stabilize metallacycles.

The results reported here are consistent with the trend noted above if we assume that a thiolate ligand is overall a much better donor of electron density to the metal than an analogous alkoxide ligand, and that greater electron donor ability alone dictates the chemistry in the phenoxide and TIPT systems discussed here. But we have some evidence that at least the second of these assumptions is in fact incorrect. $Ta(CH^tBu)(DIPP)_3(THF)$ probably reacts in an associative fashion with an olefin (at least norbornene), one that perhaps involves attack at an equatorial position next to the neopentylidene ligand in **C** (see first section). In contrast $Ta(CH^tBu)(TIPT)_3(THF)$ probably reacts dissociatively to yield incipient $Ta(CH^tBu)(TIPT)_3$ which an olefin attacks so as to produce an intermediate in which the alkylidene and the olefin are bound *trans* to one another in axial positions of the trigonal bipyramid. This *trans* TBP intermediate would have to rearrange to a *cis* intermediate in order to form the required metallacyclobutane ring. Therefore the generalization that complexes that contain thiolate ligands are poor metathesis catalysts is probably correct, but the reasons may be more subtle and varied than we anticipated initially. More studies will be required before a wholly satisfactory answer to this question is possible.

There are now several catalyst systems that will polymerize norbornene in a well-defined manner. (NBE is extremely reactive and polymerization of it by classical catalysts is well-studied;^{8,23} NBE therefore is the logical monomer for studying potentially controllable ring opening metathesis polymerization reactions by new catalysts.) The first was the titanocene system developed by Grubbs where opening of the titanacyclobutane ring is rate limiting.^{13a} The DIPP

tantalacyclobutane system we report here is remarkably similar in that respect; Grubbs reported $\Delta H^\ddagger = 27.1(0.5)$ kcal/mol, $\Delta S^\ddagger = 9(4)$ e.u., and $\Delta G^\ddagger_{338} = 24(1)$ kcal/mol compared to $\Delta H^\ddagger = 24.0(0.9)$ kcal/mol, $\Delta S^\ddagger = 4.8(2.8)$ e.u., and $\Delta G^\ddagger_{338} = 22.4(1.3)$ kcal/mol for the tantalum system. Grubbs assumed, as we have, that the *trans* to *cis* ratio in the polynorbornene results from competitive cleavage of *trans* and *cis* metallacycles, although in neither system is it possible to know what the individual rate constants for cleavage of the *trans* and *cis* metallacycles actually are. We have some evidence that the "all *cis*" tantalacycle opens significantly more rapidly than the *trans* tantalacycle, and that chain propagation is faster than chain initiation because **13** (the initiator) is *trans* while propagating tantalacycles contain a large fraction of *cis* isomer. We feel that the similarities between the tantalum DIPP system and the titanium system investigated by Grubbs are purely circumstantial; they are both well-behaved examples of catalysts in which ring-opening is rate limiting.

Several other systems are known that will polymerize norbornene. The Osborn catalyst system ($W(CHR')(OCH_2^tBu)_2(halide)_2$ /Lewis acid) has been shown to react with various norbornenes to yield living intermediates;^{13b} under some circumstances metallacycles can be observed at the same time as alkylidene complexes.^{13c} The $M(CHR')(NAr)(OR)_2$ catalyst systems ($M = Mo^7$ or W^4) can be tuned to react only with norbornene by employing $OR = t$ -butoxide. The $Mo(CHR')(NAr)(O^tBu)_2$ catalyst will tolerate ~100 equivalents of ester during the course (~15 m) of a polymerization of 5,6-dicarbomethoxynorbornene. In two cases^{4,7} the polynorbornene that is produced has been shown to be monodisperse, as one would expect for well-behaved living polymerization catalysts. Although metallacycle stability will vary widely with the degree of substitution on the ring, and the nature of the ligands in Mo and W systems, the data available so far suggest that metallacyclobutane rings become less stable toward loss of olefin (ring-opening) as one moves from group 4 to group 6 metals.

We were surprised to find such a large variation in the behavior of the three basic types of catalysts (DIPP, TIPT, DMP). Even the (presumably solely steric) differences between the DMP and DIPP ligands are extremely important if one is concerned with controlling ring-opening

polymerization reactions. The DMP catalyst system is clearly unsuitable, although we do not know why in any detail. The two most significant problems with the DIPP system are the possibility of a competitive "base one" mechanism under some conditions (equation 17), and some activity for metathesis of ordinary olefins (i.e., isomerization of the double bonds and broadening of the molecular weight distribution). The TIPT system is the best behaved overall from the practical point of view of preparing well-defined polymers through ring-opening reactions, since tantalacycles are unstable, living alkylidene complexes (containing a β proton) appear to be relatively stable (as base adducts, at least), and there is potentially a great deal of control over the rate of the ring-opening reaction by choosing the appropriate base, solvent (possibly also a coordinating ligand), and temperature. We plan to employ the thiolate catalysts in future studies of ring-opening polymerization reactions by tantalum.

Finally, we want to emphasize again the potential significance of the two quite different types of metallacyclobutane rings found in the two structures reported here. The evidence is beginning to accumulate in the tungsten alkylidene catalyst system^{21a,d} that TBP metallacyclobutane complexes are not necessarily always the most stable or even the most common. It also makes sense using both steric and electronic arguments that the short $M \cdots C_{\beta}$ distance (and concomitantly relatively large $C_{\alpha}-M-C_{\alpha}$ angle) found in TBP metallacyclic complexes must lengthen (and the $C_{\alpha}-M-C_{\alpha}$ angle must decrease) in a square pyramidal metallacyclic complex in which the ring occupies basal positions, or in an octahedral metallacyclic complex. We stress that the important question concerning how an olefin approaches a $M=C$ bond remains unanswered; our working proposal is that an olefin approaches the metal so that its C-C axis is more perpendicular than parallel to the $M=C$ bond to give a roughly square pyramidal transition state. Structures like that of 7 therefore may prove to be more relevant in that they can more readily lose an olefin to give a pseudo-tetrahedral alkylidene complex than can the more ideal trigonal bipyramidal metallacyclic complexes. The situation is more complex in this particular system because of the important role a base undoubtedly plays in several steps of a metathetical reaction.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina.

$\text{Ta}(\text{CH}_2^t\text{Bu})_2\text{Cl}_3$,^{20a} $\text{Ta}(\text{CH}^t\text{Bu})(\text{THF})_2\text{Cl}_3$,⁹ and 2,4,6- $\text{C}_6\text{H}_2^i\text{Pr}_3\text{SH}$ (HTIPT)²⁶ were prepared as described in the literature. LiDIPP- Et_2O , LiDMP, and LiTIPT were prepared from the appropriate phenol or thiol and n-butyllithium in ether (for LiDIPP- Et_2O) or pentane (for LiDMP and LiTIPT). Norbornene-2,3- d_2 was provided by J.K. Stille via R.H. Grubbs. All other reagents were purchased from commercial sources and purified by standard techniques.

Chemical shifts are listed in ppm downfield from TMS. Coupling constants are quoted in Hertz. Routine coupling constants and multiplicities are not listed. The NMR solvent is benzene- d_6 , the temperature 25°, and the field between 250 and 400 MHz (^1H), unless otherwise noted. All polymer samples were analyzed in toluene (0.3% by weight polynorbornene in solution) at 25° versus polystyrene standards (1260 - 1.030×10^6 MW) on a Waters 150C instrument equipped with three Styragel columns (10^3 , 10^4 , and 10^5 Å) and a refractive index detector. Molecular weight distributions were calculated by an accompanying Waters Data Module. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.) or Spang Microanalytical Laboratory (Eagle Harbor, Michigan).

Preparation of Compounds. $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ (DIPP = O-2,6- $\text{C}_6\text{H}_3^i\text{Pr}_2$) (1). $\text{Ta}(\text{CH}_2^t\text{Bu})_2\text{Cl}_3$ (2.00 g, 4.66 mmol) was dissolved in ether (50 mL) and the solution was cooled to -30°. THF (12 g) was added dropwise. As this solution was allowed to warm to room temperature the color changed from yellow to violet. After 2 h the solution was again cooled to -30° and stirred while solid LiDIPP- Et_2O (3.62 g, 14.0 mmol) was added. As the

solution warmed to room temperature the color changed from violet to yellow-orange. The total reaction time (including the time of addition) was 20 m. The mixture was then filtered through Celite, and the solvent was removed *in vacuo*. The resulting yellow-orange solid was dissolved in pentane, and the solution was filtered through Celite to remove any remaining LiCl. The solvent was removed *in vacuo* and the residue dissolved in ether. Orange-yellow crystals were obtained by cooling the solution to -30° (3.58 g, 90%): ^1H NMR δ 7.32 (d, 6, H_m), 7.15 (t, 3, H_p), 5.73 (s, 1, CHCMe_3), 3.99 (m, 10, CHMe_2 and THF), 1.48 (d, 36, CHMe_2), 1.31 (s plus m, 13, CHCMe_3 and THF); ^{13}C NMR δ 227.1 (d, $J_{\text{CH}} = 95$, CHCMe_3), 159.0 (s, C_{ipso}), 137.4 (s, C_o), 123.6 (d, C_m), 121.7 (d, C_p), 73.8 (m, THF), 45.0 (s, CHCMe_3), 35.7 (q, CHCMe_3), 27.1 (d, CHMe_2), 25.6 (m, THF), 24.5 (q, CHMe_2). Anal. Calcd for $\text{TaC}_4\text{H}_6\text{O}_4$: C, 63.20; H, 8.15; Cl, 0.00. Found: C, 63.13; H, 8.09; Cl, < 0.5. On a larger scale best yields are obtained if $\text{Ta}(\text{CH}^i\text{Bu})(\text{THF})_2\text{Cl}_3$ is isolated before being treated with $\text{LiDIPP}\cdot\text{Et}_2\text{O}$. **1** has been isolated in 85% yield on a 20 g scale.

$\text{Ta}(\text{CH}^i\text{Bu})(\text{DIPP})_3(\text{py})$ (2). $\text{Ta}(\text{CH}^i\text{Bu})(\text{DIPP})_3(\text{THF})$ (0.50 g, 0.58 mmol) was dissolved in ether (10 mL) and the solution was cooled to -30° . While this solution was stirred, pyridine (280 μL , excess) was added. After 10 m at 25° the solution had changed color from orange-yellow to orange. The solvent was removed *in vacuo* and the residue recrystallized from ether at -30° to give 0.38 g of orange crystals (75%): ^1H NMR δ 8.70 (py H_o), 7.06 (unresolved, H_m), 6.92 (unresolved, H_p), 6.51 (py H_p), 6.29 (CHCMe_3), 6.22 (py H_m), 3.83 (unresolved, CHMe_2), 1.22 (unresolved, CHCMe_3 and CHMe_2); ^{13}C NMR δ 231.2 (d, $J_{\text{CH}} = 96$, CHCMe_3), 157.0 (C_{ipso}), 151.0 (py C_o), 137.8 (py C_p), 137.6 (C_o), 124.4 (py C_m), 123.7 (C_m), 121.7 (unresolved, C_p), 45.2 (CHCMe_3), 35.4 (CHCMe_3), 27.1 (CHMe_2), 24.4 (CHMe_2). Anal. Calcd for $\text{TaC}_4\text{H}_6\text{NO}_3$: C, 64.08; H, 7.73. Found: C, 64.27; H, 7.78.

$\text{Ta}(\text{CH}^i\text{Bu})(\text{DMP})_3(\text{THF})$ (DMP = O-2,6- $\text{C}_6\text{H}_3\text{Me}_2$) (3). $\text{Ta}(\text{CH}^i\text{Bu})(\text{THF})_2\text{Cl}_3$ (2.00 g, 3.99 mmol) was dissolved in a mixture of ether (110 mL) and THF (10 mL), and the solution was cooled to -30° . This solution was stirred while solid LiDMP (1.53 g, 11.9 mmol) was added. While this mixture was stirred at room temperature for 20 m, LiCl precipitated and the

color changed from purple to orange-yellow. The reaction mixture was then filtered through Celite, and the solvent removed *in vacuo*. The resulting yellow-orange oil was dissolved in ether and the solution filtered again through Celite. Partial removal of the solvent *in vacuo* yielded an orange-yellow precipitate (1.25 g). An additional 0.32 g was obtained by cooling the filtrate to -30° for 12 h (total yield 57%): ^1H NMR δ 7.01 (H_m), 6.93 (CHCMe_3), 6.77 (H_p), 3.58 (THF), 2.46 (DMP Me groups), 1.15 (CHCMe_3), 1.01 (THF); ^{13}C δ 237.4 (d, $J_{\text{CH}} = 107$, CHCMe_3), 161.7 (C_{ipso}), 128.8 (C_m), 126.7 (C_o), 120.7 (C_p), 74.5 (THF), 43.1 (CHCMe_3), 36.0 (CHCMe_3), 25.3 (THF), 18.2 (DMP Me). Anal. Calcd for $\text{TaC}_{33}\text{H}_{45}\text{O}_4$: C, 57.71; H, 6.62. Found: C, 57.02; H, 6.38. Low analytical results are believed due to some decomposition in the solid state.

Ta(CH^tBu)(DMP)₃(py) (4). Pyridine (280 μL , 3.48 mmol), was added via syringe to a stirred solution of Ta(CH^tBu)(DMP)₃(THF) (0.80 g, 1.16 mmol) in ether (150 mL) at -30° . The solution was stirred at room temperature for 10 m, during which time the color changed from orange to orange-red. The solvent was removed *in vacuo* from the filtrate, and the resulting oil was dissolved in a minimal amount of a 1:1 mixture of ether and pentane. Dark yellow crystals were isolated from this solution at -30° (0.49 g, 61%): ^1H NMR δ 8.54 (py H_o), 7.51 (CHCMe_3), 7.1-6.1 (broad m, py and DMP ring protons), 2.45 (DMP Me groups), 1.25 (CHCMe_3); ^{13}C NMR δ 241.9 (d, $J_{\text{CH}} = 107$, CHCMe_3), 160.0, 128.8, 126.9, and 120.8 (DMP ring carbons), 150.9 (py C_o), 137.9 (py C_p), 124.5 (py C_m), 43.4 (CHCMe_3), 35.7 (CHCMe_3), 18.3 (DMP Me). Anal. Calcd for $\text{TaC}_{34}\text{H}_{42}\text{NO}_3$: C, 58.86; H, 6.11. Found: C, 57.70; H, 5.93. We believe decomposition of the sample is responsible for the low results.

Ta(CH^tBu)(TIPT)₃(THF) (TIPT = S-2,4,6-C₆H₂iPr₃) (5). A solution of LiTIPT (1.45 g, 5.98 mmol) in ether (25 mL) was added dropwise to a solution of Ta(CH^tBu)(THF)₂Cl₃ (1.00 g, 1.99 mmol) in ether (50 mL) at room temperature. As the solution was stirred at room temperature, the color changed from purple to orange-red. After 20 m the mixture was filtered through Celite, and the solvent was removed from the filtrate *in vacuo*. The resulting oil was dissolved in pentane, and the solution was cooled to -30° to give a yellow powder

(1.25 g, 61%): ^1H NMR δ 7.15 (H_m), 3.95 (broad septet, 6, ortho CHMe_2), 3.65 (broad, 4, THF), 2.82 (septet, 3, para CHMe_2), 1.36 (d, 36, ortho CHMe_2), 1.23 (d plus m, 22, para CHMe_2 and THF), 0.98 (s, 9, CHCMe_3); ^{13}C NMR (THF- d_8) δ 251.9 (d, $J_{\text{CH}} = 76$, CHCMe_3), 149.6, 148.9, and 148.0 (C_{ipso} , C_o and C_p), 121.1 (d, C_m), 48.3 (s, CHCMe_3), 35.2 (d, para CHMe_2), 33.0 (d, ortho CHMe_2), 31.9 (CHCMe_3), 24.8 and 24.3 (ortho and para CHMe_2). Coordinated THF resonances were assumed to be coincident with the solvent resonances. Anal. Calcd for $\text{TaC}_{54}\text{H}_{87}\text{OS}_3$: C, 62.99; H, 8.53. Found: C, 62.94; H, 8.70.

During the original workup of **5**, and upon recrystallization, small amounts of a deep red microcrystalline compound that is more soluble in pentane than **5** can be isolated. So far we have not discovered a systematic method of preparing it in high yield. Analytical, ^1H NMR, and ^{13}C NMR data are all consistent with it being " $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3$ ". We speculate that it is actually $[\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3]_2$ on the basis of the fact that it reacts only slowly with ~ 50 eq of pyridine at 50° in C_6D_6 to give **6** in $\sim 15\%$ yield in 15 m. (Related compounds of the type $\text{Mo}(\text{CCMe}_3)(\text{SAr})_3$ and $\text{W}(\text{CCMe}_3)(\text{SAr})_3$ are also believed to be dimers.¹⁹) However, if so, $[\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3]_2$ must be in rapid equilibrium with a minute amount of $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3$, since both ^1H and ^{13}C NMR spectra at room temperature show a single set of sharp TIPT resonances. We also did not find an alkylidene α carbon resonance, consistent with a monomer/dimer equilibrium of the order of the NMR time scale at room temperature and quite different chemical shifts for the alkylidene α carbon resonance in each: ^1H NMR δ 7.15 (H_m), 3.80 (ortho CHMe_2), 2.82 (para CHMe_2), 1.80 (CHCMe_3), 1.26 (para CHMe_2), 1.22 (ortho CHMe_2), 1.08 (CHCMe_3); ^{13}C NMR δ 149.4, 148.7, and 140.8 (C_{ipso} , C_o , and C_p), 121.5 (C_m), 37.5 (CHCMe_3), 34.6 (para CHMe_2), 33.8 (CHCMe_3), 33.0 (ortho CHMe_2), 24.5 and 24.2 (ortho and para CHMe_2). The C_α resonance could not be observed at room temperature. Anal. Calcd for $\text{TaC}_{50}\text{H}_{79}\text{S}_3$: C, 62.73; H, 8.32; S, 10.05. Found: C, 63.12; H, 8.29; S, 10.09.

$\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{py})$ (6). Pyridine (70 μL , 0.87 mmol) was added to a stirred solution of $\text{Ta}(\text{CH}^t\text{Bu})(\text{TIPT})_3(\text{THF})$ (0.30 g, 0.29 mmol) in ether (10 mL) at room temperature. After 20 m the solution was filtered through Celite, and the solvent was removed *in vacuo*, leaving

the product as an orange-yellow powder (0.21 g, 70%): ^1H NMR (60°) δ 6.84 (broad, H_m), 4.2–4.0 (broad, ortho CHMe_2), 4.09 (CHCMe_3), 2.72 (m, para CHMe_2), 1.38 (ortho CHMe_2), 1.24 (CHCMe_3), 1.13 (para CHMe_2); ^{13}C NMR δ 252.4 (d, $J_{\text{CH}} = 94.2$, CHCMe_3), 150.3 (py C_o), 135.2 (py C_p), 123.5 (py C_m), 150–118 (broad resonances, TIPT ring carbons), 47.1 (s, CHCMe_3), 34.5 (para CHMe_2), 32.4 (broad, ortho CHMe_2), 31.4 (CHCMe_3), 24.7 (para CHMe_2), 24.5 (broad, ortho CHMe_2). Anal. Calcd for $\text{TaC}_{55}\text{H}_{84}\text{NS}_3$: C, 63.73; H, 8.19. Found: C, 64.10; H, 8.30.

Ta[CH(Ph)CH(t Bu)CH $_2$](DIPP) $_3$ (7). A solution of styrene (200 μL , 1.74 mmol) in ether (20 mL) was cooled to -30° and added dropwise to a stirred solution of $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ (1.50 g, 1.75 mmol) in ether (40 mL) at -30° . The solution was warmed to 25° and stirred for 30 m. The deep orange solution was then filtered through Celite and the solvent removed *in vacuo* to give an orange oil. The oil was dissolved in minimal pentane and the solution was cooled to -30° to yield orange crystals (0.87 g, 57%): ^1H NMR δ 7.05 (H_m) 7.0–6.6 (m, H_p and phenyl protons), 3.47 (CHMe_2), 3.10–2.85 (m, 2, α CH_2), 2.17 (d, 1, $J_{\text{HH}} = 12$, α CHPh), 1.57 (m, 1, β CHCMe_3), 1.19 (18, CHMe_2), 1.18 (18, CHMe_2), 0.94 (CHCMe_3); ^{13}C NMR δ 157.5 (C_{ipso}), 147.9 (C_{ipso} phenyl), 138.1 (C_o), 128.2, 127.8, and 123.2 (phenyl carbons), 123.9 (C_p), 123.7 (C_m), 81.9 (d, $J_{\text{CH}} = 133$, CHPh), 63.8 (t, $J_{\text{CH}} = 129$, CH_2), 42.9 (d, $J_{\text{CH}} = 125$, CHCMe_3), 39.3 (CHCMe_3), 28.1 (CHMe_2), 27.7 (CHCMe_3), 24.0 (CHMe_2). Anal. Calcd for $\text{TaC}_{49}\text{H}_{69}\text{O}_3$: C, 66.34; H, 7.86. Found: C, 66.61; H, 7.63.

Ta(CHPh)(DIPP) $_3$ (THF) (8). A solution of styrene (110 μL , 0.96 mmol) in ether (3 mL) was cooled to -30° and added dropwise to a solution of $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ (0.80 g, 0.94 mmol) in a mixture of ether (12 mL) and THF (5 mL) at -30° . The solution was warmed to 25° and stirred for 1 h, during which time the color changed from orange-yellow to dark orange. The mixture was filtered through Celite and the solvent was removed *in vacuo* to yield a dark orange oil. The oil was dissolved in pentane and the solution was cooled to -30° to give dark orange crystals (0.37 g, 45%): ^1H NMR δ 8.49 (CHPh), 7.23 (phenyl H_m), 7.10 (H_m), 6.95–6.90 (m, H_p and phenyl H_o), 6.62 (phenyl H_p), 3.74 (m, CHMe_2 and THF), 1.23 (CHMe_2),

1.00 (m, THF); ^{13}C NMR δ 221.1 (d, $J_{\text{CH}} = 114$, CHPh), 157.9 (C_{ipso}), 145.7 (phenyl C_{ipso}), 137.7 (C_O), 129.0, 127.3, and 124.1 (unresolved, phenyl carbons), 123.6 (C_m), 122.0 (C_p), 74.9 (THF), 27.3 (CHMe_2), 25.4 (unresolved, THF), 24.3 (CHMe_2). Decomposition of **8** upon recrystallization thwarted all attempts at analysis.

Ta(CHSiMe₃)(DIPP)₃(THF) (9). A solution of trimethylsilylethylene (56 μL , 0.39 mmol) in ether (4 mL) was cooled to -30° and added dropwise to a solution of Ta(CH^{*i*}Bu)(DIPP)₃(THF) (0.30 g, 0.35 mmol) in a mixture of ether (8 mL) and THF (2 mL) at -30° . The solution was warmed to room temperature and stirred for 40 m, during which time the color changed from orange-yellow to yellow. It was filtered through Celite, and the solvent was removed *in vacuo* from the filtrate to give a yellow oil. The yield is virtually quantitative by ^1H NMR. Yellow crystals were obtained by crystallization from pentane at -30° : ^1H NMR δ 7.73 (CHSiMe_3), 7.11 (H_m), 6.94 (H_p), 3.85-3.65 (m, CHMe_2 and THF), 1.27 (CHMe_2), 1.12 (m, 4, THF), 0.17 (CHSiMe_3); ^{13}C NMR δ 210.6 (d, $J_{\text{CH}} = 102$, CHSiMe_3), 158.3 (C_{ipso}), 137.6 (C_O), 123.7 (C_m), 122.2 (C_p), 73.2 (THF), 27.2 (CHMe_2), 25.4 (unresolved, THF), 24.4 (CHMe_2), 4.08 (CHSiMe_3). Anal. Calcd for TaC₄₄H₆₉O₄Si: C, 60.66; H, 8.00. Found: C, 60.76; H, 8.01.

Ta[CH(SiMe₃)CH(SiMe₃)CH₂](DIPP)₃ (10). A solution of trimethylsilylethylene (134 μL , 0.92 mmol) in ether (4 mL) was cooled to -30° and added dropwise to a solution of Ta(CHSiMe₃)(DIPP)₃(THF) (0.40 g, 0.46 mmol) in ether (6 mL) at -30° . The solution was warmed to room temperature and stirred for 15 m, during which time the solution became colorless. Filtration through Celite followed by removal of the solvent *in vacuo* from the filtrate yielded a colorless oil. A white precipitate formed upon cooling a pentane solution to -30° (0.29 g, 71%): ^1H NMR δ 6.96 (H_m), 6.82 (m, H_p), 4.98 (t, 1, $J_{\text{HH}} = 10.1$, α CH₂), 3.64 (t, 1, $J_{\text{HH}} = 10.7$, α CH₂), 3.6-3.2 (broad, CHMe_2), 2.95 (d, 1, $J_{\text{HH}} = 14.5$, α CHSiMe₃), 1.5-0.5 (broad multiplet, CHMe_2), 0.24 (SiMe₃), 0.14 (SiMe₃), -0.33 (m, 1, β CHSiMe₃); ^{13}C NMR δ 160-120 (ring carbons), 108.1 (t, $J_{\text{CH}} = 145$, α CH₂), 99.3 (d, $J_{\text{CH}} = 128$, α CHSiMe₃), 28-22 (m, CHMe_2 and CHMe_2), 6.41 (d, $J_{\text{CH}} = 131$, β CHSiMe₃), 2.31 (SiMe₃), 0.82 (SiMe₃). Anal.

Calcd for $\text{TaC}_4\text{H}_7\text{O}_3\text{Si}_2$: C, 60.11; H, 8.18. Found: C, 60.43; H, 8.24. A small amount of another isomer (~15%), possibly $\text{Ta}[\text{CH}(\text{SiMe}_3)\text{CH}_2\text{CH}(\text{SiMe}_3)](\text{DIPP})_3$, is present according to ^1H and ^{13}C NMR spectra.

$\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{DIPP})_3$ (11a). A solution of $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ (1.50 g, 1.75 mmol) in ether (20 mL) was placed in a pressure bottle. The bottle was then pressurized at 30 psi of ethylene for 10 m, during which time the solution became nearly colorless. The solution was filtered through Celite and the solvent removed from the filtrate *in vacuo* to give a colorless oil. This oil was dissolved in pentane and the solution cooled to -30° to yield colorless crystals (0.95 g, 72%): ^1H NMR δ 6.99 (H_m), 6.84 (H_p), 3.86 (m, 4, α CH_2), 3.52 (CHMe_2), 1.12 (CHMe_2), 0.48 (m, 2, β CH_2); ^{13}C NMR δ 156.6 (C_{ipso}), 137.6 (C_o), 123.4 (C_m), 122.2 (C_p), 96.1 (t, $J_{\text{CH}} = 147$, α CH_2), 27.7 (CHMe_2), 23.8 (CHMe_2), -0.68 (t, $J_{\text{CH}} = 150$, β CH_2). Anal. Calcd for $\text{TaC}_3\text{H}_5\text{O}_3$: C, 62.05; H, 7.63. Found: C, 62.21; H, 7.58.

$\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{DIPP})_3(\text{py})$ (11b). $\text{Ta}(\text{CH}^t\text{Bu})(\text{DIPP})_3(\text{THF})$ (7.00 g, 8.19 mmol) was dissolved in ether (150 mL) and placed in a Schlenk flask sealed with a septum. The flask was attached to a Schlenk line, and ethylene was vigorously bubbled through the solution via a needle for ~60 seconds. During this time the color changed from yellow-orange to very pale yellow. The solution was then filtered through Celite, and the solvent removed from the filtrate *in vacuo*. The resulting oil was dissolved in pentane and the solution was cooled to -30° . Pyridine (1.98 mL, 24.6 mmol) was added dropwise while stirring the solution. A white precipitate formed quickly. After stirring the mixture for 10 m at room temperature this precipitate was collected and washed with cold pentane. Additional product was obtained by reducing the volume of the filtrate and cooling to -30° (total 4.90 g, 72%): ^1H NMR δ 8.58 (py H_o), 7.06 (H_m), 6.90 (H_p), 6.80 (py H_p), 6.45 (py H_m), 3.57 (CHMe_2), 2.95 (m, 4, α CH_2), 2.00 (m, 2, β CH_2), 1.15 (CHMe_2); ^{13}C NMR δ 156.6 (C_{ipso}), 150.1 (py C_o), 138.0 (C_o), 136.0 (unresolved, py C_p), 123.8 (py C_m), 123.6 (C_m), 122.3 (C_p), 78.0 (t, $J_{\text{CH}} = 120$, α CH_2), 36.3 (t, $J_{\text{CH}} = 129$, β CH_2), 27.6 (CHMe_2), 24.0 (CHMe_2). Anal. Calcd for $\text{TaC}_4\text{H}_6\text{NO}_3$: C, 63.37; H, 7.49. Found: C, 63.85; H, 8.05.

Ta[CH(C₅H₈)CHCH(^tBu)](DMP)₃ (12). A solution of norbornene (0.055 g, 0.58 mmol) in ether (20 mL) was cooled to -30° and added to a solution of Ta(CH^tBu)(DMP)₃(THF) (0.40 g, 0.58 mmol) in ether (40 mL) at -30°. The solution rapidly turned from orange-yellow to yellow. After 15 m at -30° the solvent was removed *in vacuo* to give a yellow oil. This oil was taken up in pentane and the solution was cooled to -30° to yield a pale yellow precipitate (0.13 g, 31%). A ¹H NMR spectrum of the crude oil showed the product to be formed in high yield; the low isolated yield is thought to arise from the high solubility of the compound: ¹H NMR δ 6.8 (H_m), 6.62 (H_p), 5.21 (d, 1, J_{HH} = 9.6, α CHC₅H₈), 3.72 (d, 1, J_{HH} = 10.0, α CHCMe₃), 2.86 and 2.80 (each a broad d, 1 each, CH's of C₅H₈), 2.21 (DMP Me groups), 1.7–1.4 (m, 4, CH₂'s of C₅H₈), 1.35 and 0.60 (each a broad d, 1 each, bridgehead H's of C₅H₈), 1.16 (CMe₃), 0.84 (t, J_{HH} = 9.1, β C₅H₈CH); ¹³C NMR δ 159.6 (C_{ipso}), 135.0 and 132.5 (each a d, J_{CH} = 142 and 132, α C's), 128.5 (C_m), 127.1 (C_o), 121.2 (C_p), 45.7 and 45.0 (each a d, CH's of C₅H₈), 38.6 (CMe₃), 34.5 and 34.6 (each a t, CH₂'s of C₅H₈), 33.1 (CMe₃), 30.2 (t, bridgehead C of C₅H₈), 29.0 (d, J_{CH} = 149, β C₅H₈CH), 18.0 (DMP Me). We were never able to obtain a satisfactory elemental analysis, presumably because of sample decomposition (as judged visually).

Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃ (13). A solution of norbornene (0.077 g, 0.82 mmol) in ether (10 mL) was added to a stirred solution of Ta(CH^tBu)(DIPP)₃(THF) (0.70 g, 0.82 mmol) in ether (30 mL) at -30°. The reaction rapidly turned colorless from yellow-orange. The solution was stirred at room temperature for 30 m, and the solvent was removed *in vacuo* to yield a white powder. Crystallization from ether yielded a microcrystalline white powder (0.46 g, 64%): ¹H NMR δ 7.1–6.8 (m, H_m and H_p), 5.32 (d, 1, J_{HH} = 9.6, α CHC₅H₈), 3.88 (d, 1, J_{HH} = 10.1, α CHCMe₃), 3.8–3.2 (broad, CHMe₂), 3.00 and 2.82 (each a broad s, 1 each, CH's of C₅H₈), 0.88 (broad t, 1, J_{HH} unresolved, β C₅H₈CH), 1.6–0.5 (broad; no other specific assignments could be made); a ¹³C NMR spectrum at room temperature displayed broad resonances. Anal. Calcd for TaC₄₈H₇₁O₃: C, 65.72; H, 8.18. Found: C, 65.90; H, 8.36.

Ta[CH(C₅H₈)CHCH(CHC₅H₈CH=CH^tBu)](DIPP)₃ (15). A solution of norbornene (0.083 g, 0.88 mmol) in ether (20 mL) was cooled to -30° and added to a solution of

Ta(CH^tBu)(DIPP)₃(THF) (0.750 g, 0.88 mmol) in ether (30 mL) at -30°. The solution was warmed to room temperature and the solvent removed *in vacuo* after 20 m. The off-white solid was dissolved in toluene (10 mL), and norbornene (0.083 g, 0.88 mmol) in toluene (10 mL) was added. This solution was heated to 60° for 25 m. The solution was filtered through Celite, and the solvent was removed *in vacuo*, leaving behind a colorless oil. This oil was taken up in pentane (it is *extremely* soluble), and the solution was filtered through Celite to remove any undissolved Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃. After standing the solution for several days at -30°, a white precipitate was collected (0.34 g, 40%): ¹H NMR δ 6.99 (br d, H_m), 6.84 (br t, H_p), 5.6–5.3 (m, 2, olefinic H's), 5.23 (d, 1, J_{HH} = 9.1, α CHC₅H₈), 3.85 (t, 1, J_{HH} = 8.6, α CH(C₅H₈)CHCH(^tBu)), 3.8–3.1 (broad, CHMe₂), 1.12 (CMe₃). All other resonances were broad and complex, so no other specific assignments could be made. This product is not pure, the major impurity being Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃ according to ¹H NMR spectra.

Ta[CH₂CH₂CH₂CH(Ph)O](DIPP)₃(py) (17). A solution of benzaldehyde (61 μL, 0.60 mmol) in ether (5 mL) was cooled to -30° and added to a solution of Ta(CH₂CH₂CH₂)(DIPP)₃(py) (0.50 g, 0.60 mmol) in ether (15 mL) at -30°. The solution was held at -30° for 15 m and then 25° for an additional 60 m. A white solid precipitated from the solution but redissolved when the solution reached room temperature. The solution was filtered through Celite and the solvent removed *in vacuo* to give a white solid that was reprecipitated from pentane at -30° (yield 0.45 g, 80%): ¹H NMR δ 8.64 (broad s), 7.15–6.85 (m, 6), 7.08 (d, 6), 6.93 (t, 3), and 6.61 (t, 2, all pyridine, phenyl, or DIPP ring resonances), 5.56 (d of d, 1, J_{HH} = 2.6 and 10.4, CHPh), 3.66 (CHMe₂), 3.2–1.6 (m, 6, α CH₂, β CH₂, and γ CH₂), 1.16 (18, CHMe₂), 1.14 (18, CHMe₂); ¹³C NMR δ 157.0 (s), 150.2 (d), 144.8 (s), 138.0 (s), 135.6 (d), 129–125.6 (unresolved), 123.7 (d), and 122.7 (d, all pyridine, phenyl, or DIPP ring carbons), 85.1 (d, J_{CH} = 144, CHPh), 66.2 (t, J_{CH} = 120, α CH₂), 42.0 (t, J_{CH} = 126, β CH₂), 27.6 (t, J_{CH} = 127, γ CH₂), 27.4 (CHMe₂), 24.3 (CHMe₂), 24.0 (CHMe₂). Anal. Calcd for TaC₅₁H₆₈NO₄: C, 65.15; H, 7.31. Found: C, 64.74; H, 6.87.

Ta[CH₂CH₂CH₂C(Me)₂O](DIPP)₃ (18). A solution of acetone (7.3 μ L, 0.10 mmol) in ether (5 mL) was cooled to -30° and added to a solution of Ta(CH₂CH₂CH₂)(DIPP)₃ (0.075 g, 0.10 mmol) in ether (5 mL) at -30°. The solution was held at -30° overnight, during which time the color did not change and no precipitate was observed. Filtration of the solution followed by removal of the solvent *in vacuo* yielded a colorless oil in essentially quantitative yield by ¹H NMR; the compound can be obtained as a white precipitate when the reaction is performed on a larger scale: ¹H NMR δ 7.06 (H_m), 6.91 (H_p), 3.59 (CHMe₂), 2.40 (broad, 2, α CH₂), 2.23 (broad, 2, β CH₂), 1.52 (broad, 2, γ CH₂), 1.22 (CHMe₂), 0.97 (CMe₂); ¹³C NMR δ 157.5 (C_{ipso}), 137.5 (C_o), 123.6 (C_m), 122.5 (C_p), 82.1 (s, CMe₂), 66.9 (t, J_{CH} = 122, α CH₂), 45.4 (t, J_{CH} = 123, β CH₂), 37.5 (CMe₂), 29.5 (CHMe₂), 27.4 (CHMe₂), 23.9 (t, J_{CH} = 127, γ CH₂). Anal. Calcd for TaC₄₂H₆₃O₄: C, 62.06; H, 7.81. Found: C, 61.99; H, 7.95.

Ta[CH₂CH₂CH₂CH(^tBu)O](DIPP)₃ (19). Pivaldehyde (29 μ L, 0.27 mmol) was added to a stirred solution of Ta(CH₂CH₂CH₂)(DIPP)₃ (0.20 g, 0.26 mmol) in ether (5 mL) at -30°. After standing the reaction mixture overnight at room temperature, the solvent was removed *in vacuo*, leaving behind a colorless oil in essentially quantitative yield by NMR. The product could not be obtained in crystalline form, even when the reaction was performed on a large scale: ¹H NMR δ 7.07 (H_m), 6.92 (H_p), 4.09 (d of d, 1, J_{HH} = 1.9 and 11.4, CHCMe₃), 3.58 (CHMe₂), 3.11 (m, 1, α CH₂), 2.63 (d of t, 1, J_{HH} unresolved, α CH₂), 1.9–1.5 (multiplet, 4, β CH₂ and γ CH₂), 1.23 (18, CHMe₂), 1.19 (18, CHMe₂), 0.71 (CHCMe₃); ¹³C NMR δ 157.1 (C_{ipso}), 137.7 (C_o), 123.6 (C_m), 122.7 (C_p), 91.8 (d, J_{CH} = 140, CHCMe₃), 66.8 (t, J_{CH} = 123, α CH₂), 35.1 (CHCMe₃), 33.3 (t, J_{CH} = 123, β CH₂), 27.6 (t, J_{CH} = 129, γ CH₂), 27.4 (CHMe₂), 26.0 (CHCMe₃), 24.3 (CHMe₂), 24.1 (CHMe₂).

X-Ray structure of Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃ (7). Data were collected at -65° on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo K α radiation. Axial photographs were taken on the diffractometer about each of the reciprocal axes to check that the unit cell lengths were correct. The program TRACER run on the unit cell (which was calculated with 25 high angle reflections ($2\theta >$

30°)) revealed no higher symmetry. Data collection, reduction, and refinement procedures can be found elsewhere.²⁷ A total of 11816 reflections were collected in the range $3^\circ < 2\theta < 45^\circ$ with the 7831 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was carried out in two blocks (224 variables each) using SHELX-76. Final $R_1 = 0.084$ and $R_2 = 0.115$. A semiempirical absorption correction was applied ($\mu = 5.8 \text{ cm}^{-1}$). Two crystallographically independent but closely analogous molecules are present in the asymmetric unit. Only the Ta atoms were refined anisotropically. Most hydrogen atoms could be placed in calculated positions ($\text{C-H} = 0.95 \text{ \AA}$) and constrained to ride on their respective carbon atoms. Hydrogen atoms on the TaC_3 ring carbon atoms could not be located and were ignored. A final difference Fourier map showed no significant features. The crystal data are the following: space group $P2_1/n$ with $a = 21.338(11) \text{ \AA}$, $b = 11.699(5) \text{ \AA}$, $c = 37.198(23) \text{ \AA}$, $\beta = 102.66(5)^\circ$, $Z = 8$, $M_r = 887.03 \text{ g}$, $V = 9060.1 \text{ \AA}^3$, $\rho(\text{calcd}) = 1.301 \text{ g cm}^{-3}$.

X-Ray structure of $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(\text{tBu})](\text{DIPP})_3$ (13). Data were collected at -65° on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low temperature device and using $\text{Mo K}\alpha$ radiation. Data collection, reduction, and refinement procedures have been detailed elsewhere.²⁷ A total of 7749 reflections ($+h, +k, \pm l$) were collected in the range $3^\circ \leq 2\theta \leq 50^\circ$ with the 4679 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (278 variables) using SHELX-76 with final $R_1 = 0.068$ and $R_2 = 0.061$. The tantalum and all the non-hydrogen atoms of the metalacyclobutane ring were refined anisotropically. All remaining non-hydrogen atoms in the complex were refined isotropically. The three hydrogen atoms on the metalacyclobutane ring were omitted, but all remaining hydrogen atoms were placed in calculated positions and were constrained to ride on their respective carbon atoms. A final difference-Fourier map showed no chemically significant features. The crystal data are the following: space group $P2_1/n$, $a = 11.587(4) \text{ \AA}$, $b = 20.795(4) \text{ \AA}$, $c = 18.388(4) \text{ \AA}$, $Z = 4$, $M_r = 877.03 \text{ g}$, $V = 4416.6 \text{ \AA}^3$, $\rho(\text{calcd}) = 1.319 \text{ g cm}^{-3}$, $\mu = 24.0 \text{ cm}^{-1}$. A semi-empirical absorption correction was applied.

Preparation of Polynorbornene with 5, 6, 12, and 13. In a typical reaction, a solution of 13 (20 mg) in toluene was mixed with a solution of norbornene in toluene such that the total volume was 15-20 mL. The resulting solution was heated in an oil bath to 65°, and the reaction monitored by GLC. After all norbornene was consumed, excess benzaldehyde or acetone (~50 μ L) was added, and the mixture was heated to 65° for another 15 minutes. The solvent was removed *in vacuo* and the polymer sample was rinsed with 20-30 mL methanol (containing a small amount of BHT, 2,6-di-*t*-butyl-4-methylphenol) and dried *in vacuo*. When 5 was employed as the catalyst, the polymerization and capping reactions were done at 25°.

Kinetics of Polymerization of Norbornene. Stock solutions of norbornene in benzene- d_6 and the catalyst (e.g., 13) in benzene- d_6 (with a few equivalents of mesitylene as internal standard) were prepared. In a typical run, aliquots of each solution were added to an NMR tube and additional benzene- d_6 added such that the total volume was 1 mL. The NMR tube was sealed and kept at -30°. The sample was placed in the probe of a Varian XL-300 NMR spectrometer maintained at the reaction temperature (determined before and after the run with ethylene glycol). After allowing 10 m for equilibration of the sample, and after all the initial 13 had been consumed, the disappearance of the olefinic protons of norbornene was monitored relative to the internal standard. A plot of [NBE] versus time gave k_{obs} , where $k_{obs} = k_1[13]$. All runs were monitored for at least 3 half lives, and in all cases acceptable R values were obtained from the subsequent kinetic plots. An analogous procedure was employed for the reactions of 12 and 6 with norbornene, except that the signal from C_6D_5H was utilized as the internal standard. For 6, a plot of $\ln[NBE]$ versus time gave $k_{obs}[6]$. For the reaction of 15 with NBE-2,3- d_2 , samples were prepared as described above employing stock solutions of NBE-2,3- d_2 in toluene- d_8 and 15 in benzene- d_6 . The rate of ring opening of 15 was determined by monitoring the disappearance of the α proton at 5.23 ppm.

Capping Living Polymers; Spin Simulation Experiments. A sample of 14 ($x_{avg} = 7$) was treated with three equivalents of benzaldehyde in C_6D_6 at 65°. A 1H NMR spectrum of the resulting $PhH_A C=CH_B [C_5H_8CH=CH]_x tBu$ displayed olefinic resonances in the region 6.0-

6.5 ppm for H_A and H_B (Figure 5b). Based on related studies²⁸ in which only the *trans* isomer (of the phenyl substituted capping olefin group) is observed, the resonances at 6.38 and 6.33 were assigned to H_A , and those at 6.18-6.10 ppm were assigned to H_B of the *trans* isomer. Using the values $\delta H_A = 1905$ Hz and $\delta H_B = 1841$ Hz at 300 MHz, $J_{AB} = 16$ Hz and $J_{BX} = 8$ Hz (H_X is the first cyclopentyl tertiary proton), a theoretical spectrum for the *trans* isomer was calculated (Figure 6a), utilizing a software program based on the iterative spin simulation program LAME. The results of the calculated spectrum suggest that resonances for H_{Acis} isomer overlap with those for H_{Atrans} isomer between 6.30 and 6.45 ppm in the observed spectrum (Figure 6b). The resonances for H_{Bcis} isomer are assumed to occur upfield of those for H_{Btrans} resonances at 6.18-6.10 ppm and are obstructed by polynorbornene resonances at ~5.2-5.6 ppm. This type of shift is generally observed for an olefinic proton *trans* to a phenyl group (H_{Bcis}) relative to one *cis* to a phenyl group (H_{Btrans}). For example, using a general formula,²⁹ H_{Bcis} is calculated to resonate at 5.62 ppm, while H_{Btrans} is calculated to resonate at 6.09 ppm, consistent with what we propose. Utilizing the above data the *trans/cis* capped polymer ratio can be easily determined by comparing the integrations of the resonances at 6.30-6.45 ppm (H_{Atrans} plus H_{Acis}) with those for the resonances at 6.18-6.10 ppm (H_{Btrans}). In this way the double bond formed by reaction of 14 with benzaldehyde was determined to be 68% *trans* and 32% *cis*. In an analogous manner the terminal double bond formed by reaction of $Ta[(CHC_5H_8CH)_xCH^tBu](TIPT)_3(THF)$ ($x_{avg} = 10$) with 3 eq of benzaldehyde in C_6D_6 at 25° was determined to be 64% *cis* and 36% *trans*.

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Supplementary Material Available: Tables of final atomic coordinates and temperature factors, a listing of observed and calculated structure factors, and a fully labelled figure for $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(\text{tBu})](\text{DIPP})_3$. Supplementary material for $\text{Ta}[\text{CH}(\text{Ph})\text{CH}(\text{tBu})\text{CH}_2](\text{DIPP})_3$ was provided in the preliminary communication.^{14a} Ordering information is given on any current masthead page.

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Table I. NMR Data for the Alkylidene Ligands in Tantalum Alkylidene Complexes of the Type $\text{Ta}(\text{CHR})\text{X}_3(\text{S})$.^a

Cmpd	CHR	X	S	δH_α	δC_α	J_{CH}
1	CH^tBu	DIPP	THF	5.73	227.1	95
2	CH^tBu	DIPP	py	6.29	231.2	96
3	CH^tBu	DMP	THF	6.93	237.4	107
4	CH^tBu	DMP	py	7.51	241.9	107
5	CH^tBu	TIPT	THF	c	251.9 ^b	76
6	CH^tBu	TIPT	py	4.09	252.4	94
8	CHPh	DIPP	THF	8.49	221.1	114
9	CHSiMe_3	DIPP	THF	7.73	210.6	102
16	CHR	DIPP	THF	7.69 ^b		

^a Solvent = C_6D_6 and $\text{T} = 25^\circ$ unless otherwise noted.

^b THF- d_8

^c Not observed.

Table II. Proton and Carbon NMR Data for the TaC₃ Ring in Tantalacyclobutane Complexes.^a

Compound	H _α	H _β	C _α (J _{CH})	C _β (J _{CH})
Ta[CH(Ph)CH(^t Bu)CH ₂](DIPP) ₃ (7)	3.10-2.85(2) 2.17(1)	1.57	81.9(d, 133) 63.8(t, 129)	42.9(125)
Ta[CH(SiMe ₃)CH(SiMe ₃)CH ₂](DIPP) ₃ (10)	4.98(t) 3.64(t) 2.95(d)	-0.33	108.1(t, 145) 99.3(d, 128)	6.41(131)
Ta(CH ₂ CH ₂ CH ₂)(DIPP) ₃ (11a)	3.86	0.48	96.1(147)	-0.68(150)
Ta(CH ₂ CH ₂ CH ₂)(DIPP) ₃ (py) (11b)	2.95	2.00	78.0(120)	36.3(129)
Ta[CH(C ₅ H ₈)CHCH(^t Bu)](DMP) ₃ (12)	5.21(H ₁) 3.72(H ₂)	0.84(H ₃)	132.5(132) 135.0(142)	30.2 or 29.0(149 ^b)
Ta[CH(C ₅ H ₈)CHCH(^t Bu)](DIPP) ₃ (13)	5.32(H ₁) 3.88(H ₂)	0.88(H ₃)		
Ta[CH(C ₅ H ₈)CHCH(C ₅ H ₈ CH=CH ^t Bu)]-(DIPP) ₃ (15)	5.23(H ₁) 3.85(H ₂)	obscured		

^a Solvent = C₆D₆ and T = 25° unless otherwise noted.

^b For 29.0 ppm resonance.

Table III. Selected Bond distances (Å) and Angles (°) in Ta[CH(Ph)CH(^tBu)CH₂](DIPP)₃ (7).

Ta-O(11)	1.893(13)	O(21)-Ta-O(31)	120.2(7)
Ta-O(21)	1.820(14)	C(41)-Ta-O(11)	90.3(7)
Ta-O(31)	1.864(15)	C(41)-Ta-O(21)	106.7(7)
Ta-C(41)	2.168(24)	C(41)-Ta-O(31)	128.8(7)
Ta...C(42)	2.782(24)	C(43)-Ta-O(11)	150.9(8)
Ta-C(43)	2.188(24)	C(43)-Ta-O(21)	96.7(7)
C(41)-C(42)	1.593(30)	C(43)-Ta-O(31)	89.3(8)
C(42)-C(43)	1.473(36)	C(43)-Ta-C(41)	64.4(9)
Ta-C(41)-C(42)	94.2(1.4)	C(41)-C(42)-C(43)	98.4(18)
Ta-C(43)-C(42)	97.0(1.5)	Ta-O(11)-C(11)	157.0(13)
O(11)-Ta-O(21)	104.7(6)	Ta-O(21)-C(21)	154.5(13)
O(11)-Ta-O(31)	96.6(6)	Ta-O(31)-C(31)	146.3(15)

Table IV. Products of the Reactions of Tantalacyclobutane Complexes with Organic Carbonyls.

<u>Compound</u>	<u>Carbonyl</u>	<u>Conditions</u>	<u>Insertion (%)</u>	<u>Wittig (% by NMR)</u>
7	1.5 Me ₂ CO	C ₆ D ₆ , 25°, 60 m	a	86 (Me ₂ C=CCHPh) 91 (^t BuCH=CH ₂)
11a	1.5 Me ₂ CO	C ₆ D ₆ , 25°, 60 m	100 (NMR)	b
11a	1.5 Me ₂ CO	C ₆ D ₆ , 60°, 30 m	75 (NMR)	19 (Me ₂ C=CH ₂)
11a	1.0 ^t BuCHO	ether, 25°, 12 h ^c	100 (NMR)	b
11a	1.5 Ph ₂ CO	C ₆ D ₆ , 25°, 60 m	45 (NMR)	46 (Ph ₂ C=CH ₂)
11a	1.5 Ph ₂ CO	C ₆ D ₆ , 60°, 30 m	24 (NMR)	71 (Ph ₂ C=CH ₂)
11b	1.5 Me ₂ CO	ether, 25°, 45 m ^c	100(NMR)	b
11b	1.0 PhCHO	ether, 25°, 60 m ^c	80 (isolated)	b
11b	1.2 ^t BuCHO	C ₆ D ₆ , 25°, 30 m	100 (NMR)	b
11b	1.5 Ph ₂ CO	C ₆ D ₆ , 70°, 35 m	< 6 (NMR)	86 (Ph ₂ C=CH ₂)

^a No insertion products observed by NMR.

^b No Wittig products observed.

^c Reaction was initiated at -30°.

Table V. Selected Bond distances (Å) and Angles (°) in Ta[CH(C₅H₈)CHCH(^tBu)](DIPP)₃ (**13**).

Ta-O(1)	1.917(8)	O(2)-Ta-O(3)	87.5(3)
Ta-O(2)	1.904(9)	C(41)-Ta-O(1)	89.2(5)
Ta-O(3)	1.909(8)	C(41)-Ta-O(2)	136.1(5)
Ta-C(41)	2.138(14)	C(41)-Ta-O(3)	93.1(5)
Ta...C(42)	2.382(16)	C(43)-Ta-O(1)	95.3(4)
Ta-C(43)	2.144(13)	C(43)-Ta-O(2)	145.1(6)
C(41)-C(42)	1.546(22)	C(43)-Ta-O(3)	88.9(4)
C(42)-C(43)	1.553(21)	C(43)-Ta-C(41)	78.7(7)
Ta-C(41)-C(42)	78.8(9)	C(41)-C(42)-C(43)	122.4(13)
Ta-C(43)-C(42)	78.4(8)	Ta-O(1)-C(11)	161.0(8)
O(1)-Ta-O(2)	88.1(3)	Ta-O(2)-C(21)	159.3(8)
O(1)-Ta-O(3)	175.5(3)	Ta-O(3)-C(31)	163.7(7)

Table VI. The Results of GPC Analysis of Polynorbornenes.

Run	Catalyst	Equiv. NBE	M_n (uncorr)	M_w/M_n
1	13	100	22,000	1.63
2	13	200	48,000	1.66
3	13	500	127,000	1.73
4a,b	13	200	32,100	1.04
5d	13	150	31,500	1.95
6	5	50	13,200	1.08
7	5	100	26,200	1.09
8	5	200	58,800	1.10
9	6	95	18,800	1.07
10	12	100	10,700	2.71
11	1	200	146,000	4.41
12 ^c	5	200	59,100	1.05
13 ^c	5	200	57,600	1.07

^a The reaction was taken to ~75% completion.

^b The polymer with the expected molecular weight made up ~94% of the sample; ~6% of a fraction with a relatively high molecular weight could be resolved as a separate peak in this GPC trace.

^c A sample for run 12 was taken after 20 minutes, at which time the polymerization was complete; a sample for run 13 was taken from the same reaction after 55 minutes.

^d The reaction was heated at the polymerization temperature for several extra hours after all of the NBE had been consumed.

Table VII. Kinetic Data for the Polymerization of NBE by 13 and 6.

Catalyst	[Ta] (mM)	[NBE] ₀ (mM)	T (K)	k x 10 ³
13	10.9	111	308.4	0.64 s ⁻¹
13	5.59	80	317.9	2.0 s ⁻¹
13	5.59	55	323.3	3.5 s ⁻¹
13	6.84	183	323.3	3.9 s ⁻¹
13	7.98	189	323.3	3.9 s ⁻¹
13	2.91	46	323.3	3.8 s ⁻¹
13	5.59	45	330.0	7.1 s ⁻¹
13	5.70	177	330.0	7.6 s ⁻¹
13	9.32	87	333.1	12 s ⁻¹
13	5.59	200	337.8	23 s ⁻¹
6	9.08	166	313.0	48 M ⁻¹ s ⁻¹
6	9.08	134	322.2	80 M ⁻¹ s ⁻¹
6	17.8	199	322.4	94 M ⁻¹ s ⁻¹
6	18.1	122	323.1	79 M ⁻¹ s ⁻¹
6 ^a	19.3	272	323.0	0.2 M ⁻¹ s ⁻¹

^a Polymerization carried out in the presence of 3 eq of pyridine and monitored over ~1 half life.

Figure Captions

Figure 1. A view of $\text{Ta}[\text{CH}(\text{Ph})\text{CH}(\text{}^t\text{Bu})\text{CH}_2](\text{DIPP})_3$ (**7**) (molecule **1**). Spheres of arbitrary radius are employed in order to allow a clear view of the ligand system.

Figure 2. A comparison of metallacyclobutane rings in $\text{W}[\text{CH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{CH}_2](\text{N}-2,6\text{-C}_6\text{H}_3\text{}^i\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$, **7**, and **13**.

Figure 3. The ^1H NMR Spectrum of $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(\text{}^t\text{Bu})](\text{DMP})_3$ (**12**) in C_6D_6 (* = diethyl ether).

Figure 4. A view of $\text{Ta}[\text{CH}(\text{C}_5\text{H}_8)\text{CHCH}(\text{}^t\text{Bu})](\text{DIPP})_3$ (**13**).

Figure 5. The ^1H NMR Spectrum of **14** in C_6D_6 at 50° (* = mesitylene internal standard).

Figure 6. (a) Calculated spectrum for the olefinic protons in the *trans* phenyl-substituted portion of the Wittig product produced upon treating **14** with benzaldehyde. (b) Experimental spectrum for the olefinic protons in the phenyl-substituted cap in the Wittig product produced upon treating **14** with benzaldehyde. (See Experimental Section for details.)

Figure 7. A plot of the consumption of 20 equivalents of NBE by **13** at 50° in C_6D_6 .

Figure 8. The ^1H NMR spectrum of **6** after reaction with ~15 eq of NBE in C_6D_6 at 50° (* = NBE).

Figure 9. GPC traces for the benzylidene-capped polynorbornene produced by adding 100 eq of NBE to **5** (a) (polydispersity 1.09) and **13** (b) (polydispersity 1.63).

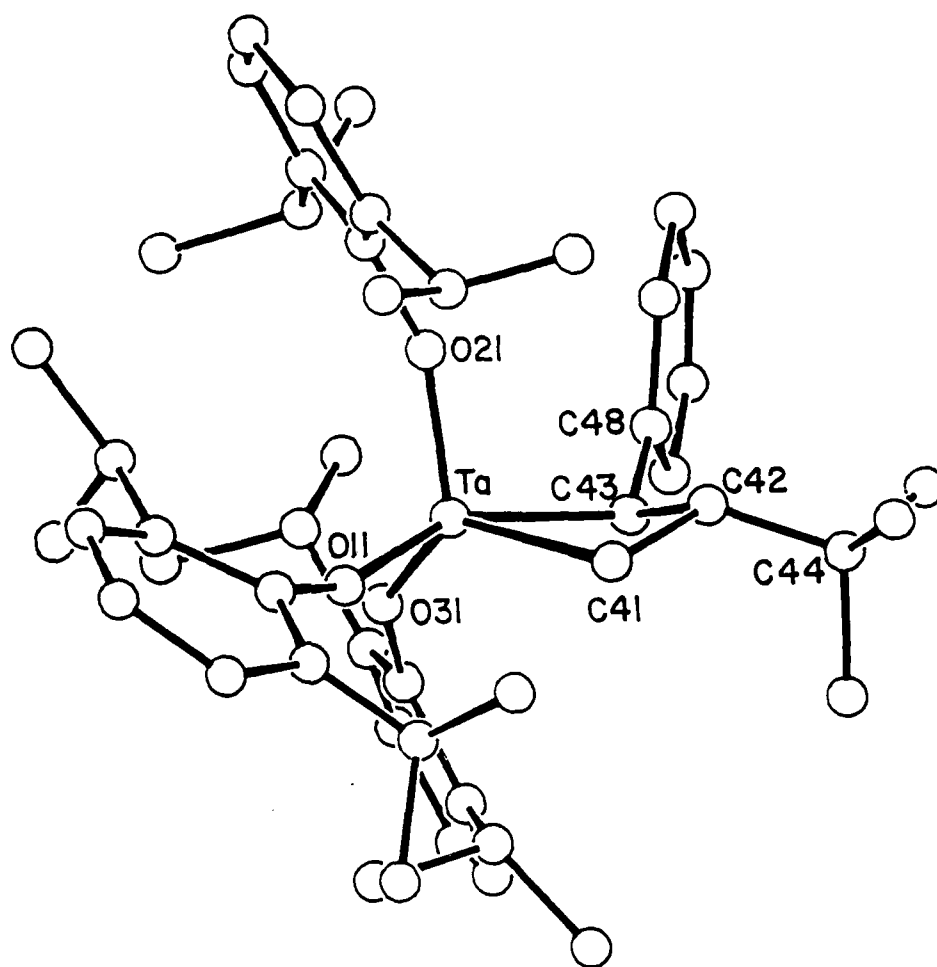


Fig. 1

Figure 2

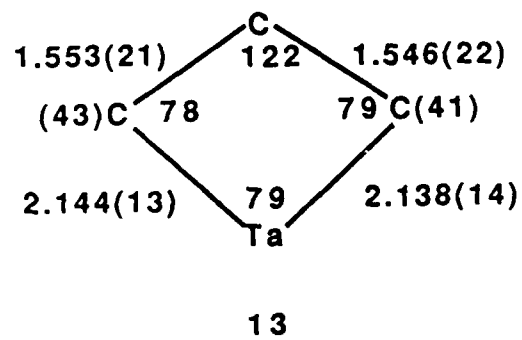
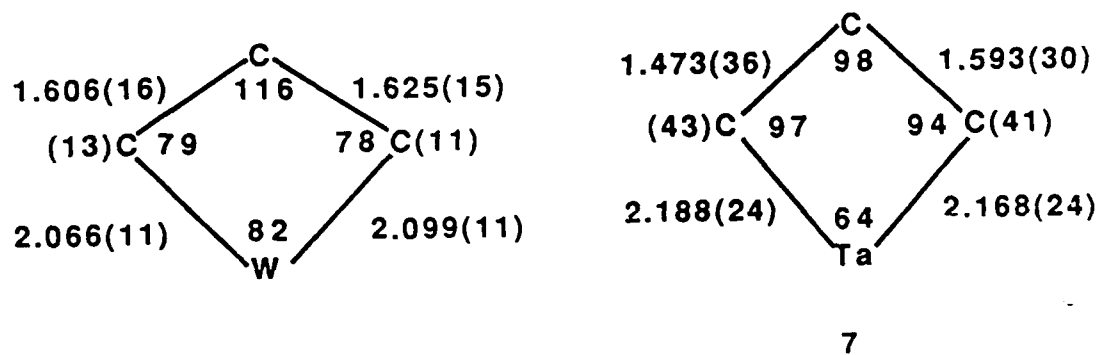
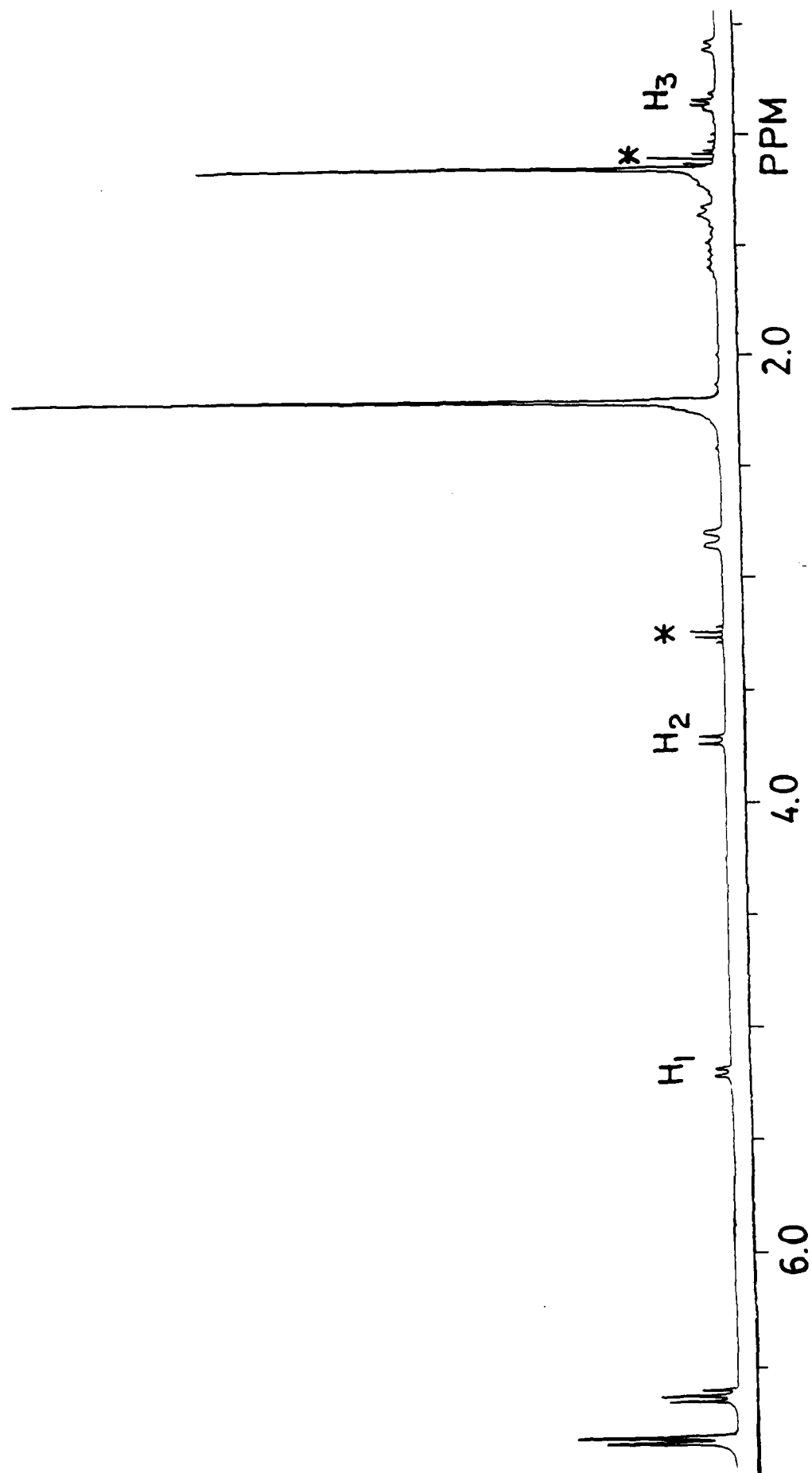


Fig. 3



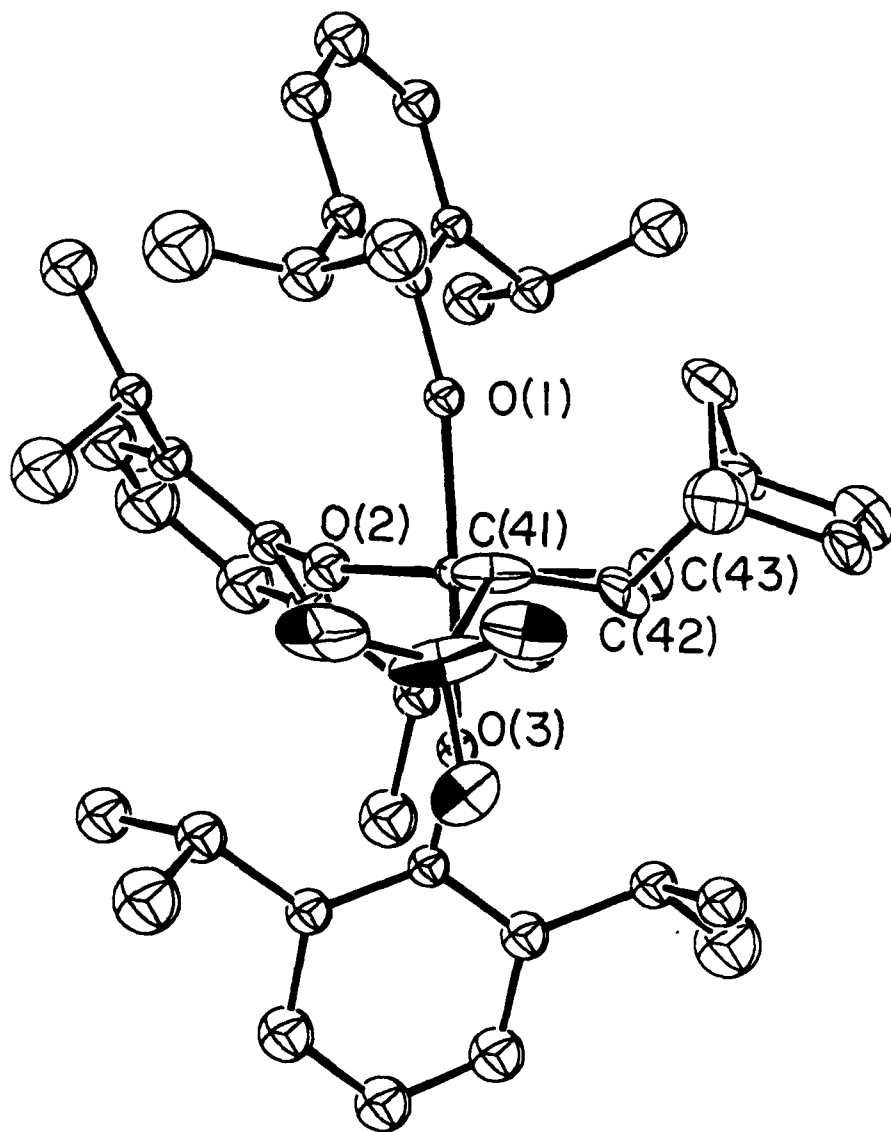


Figure 5

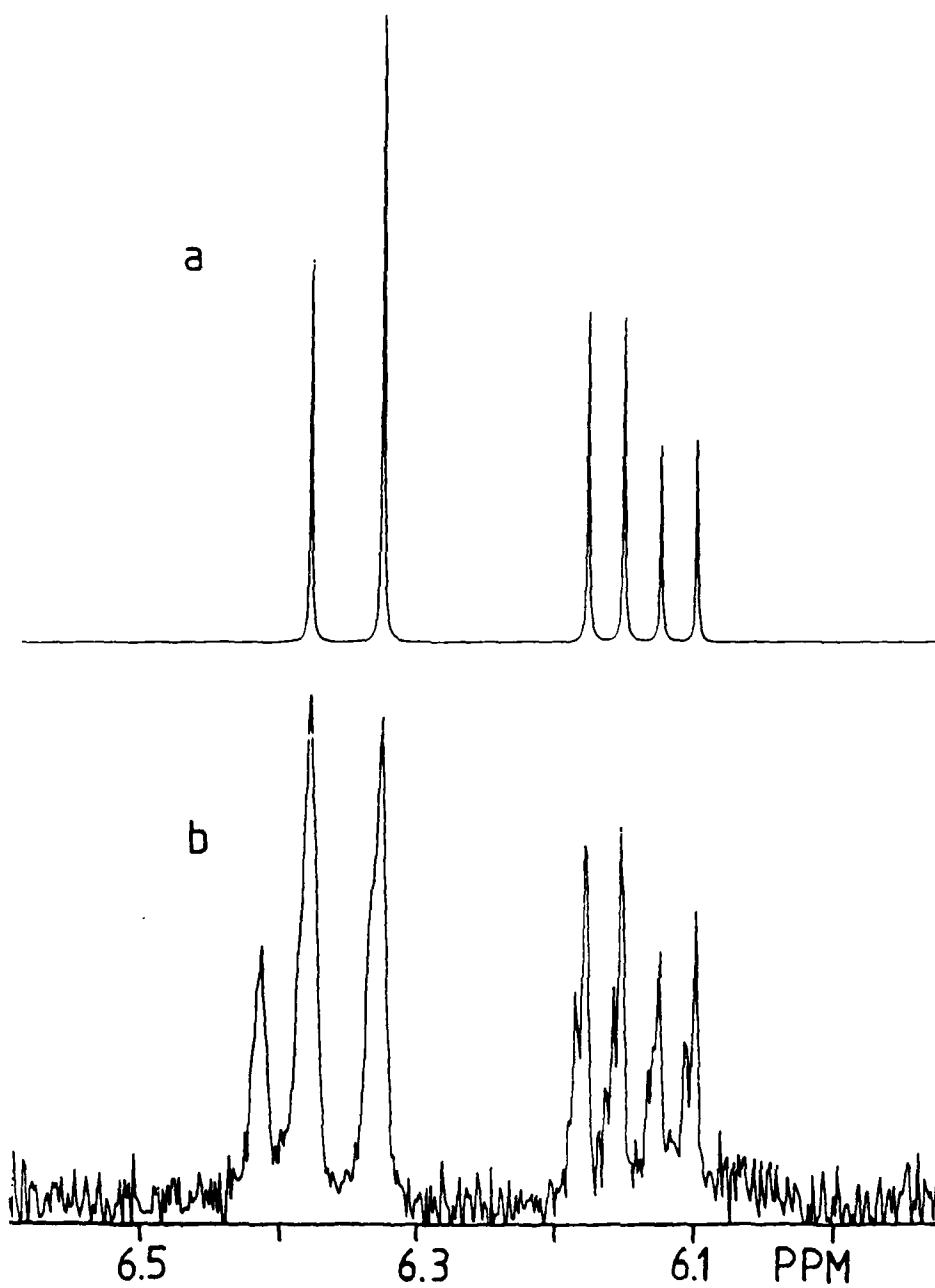


Fig 6a

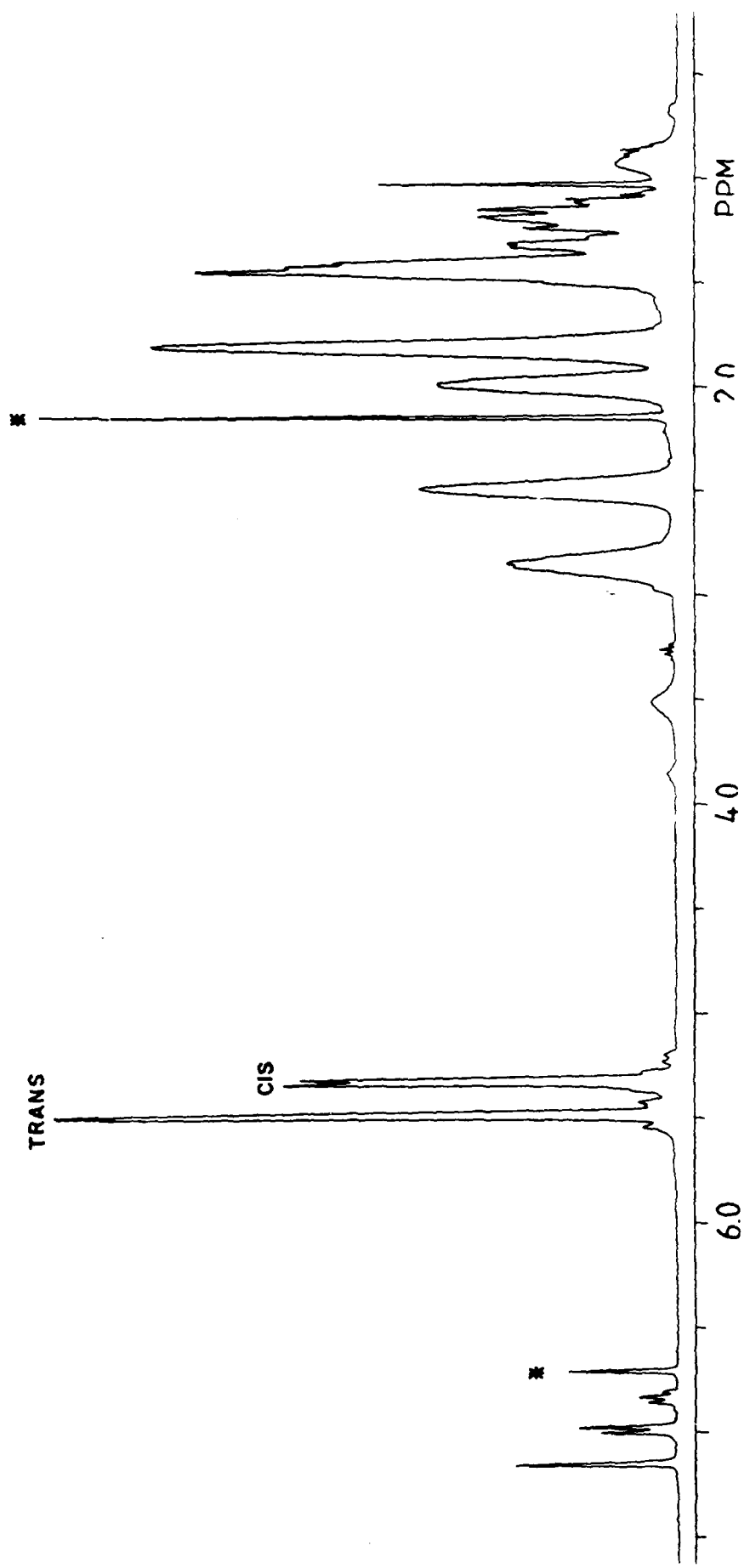


Figure 7

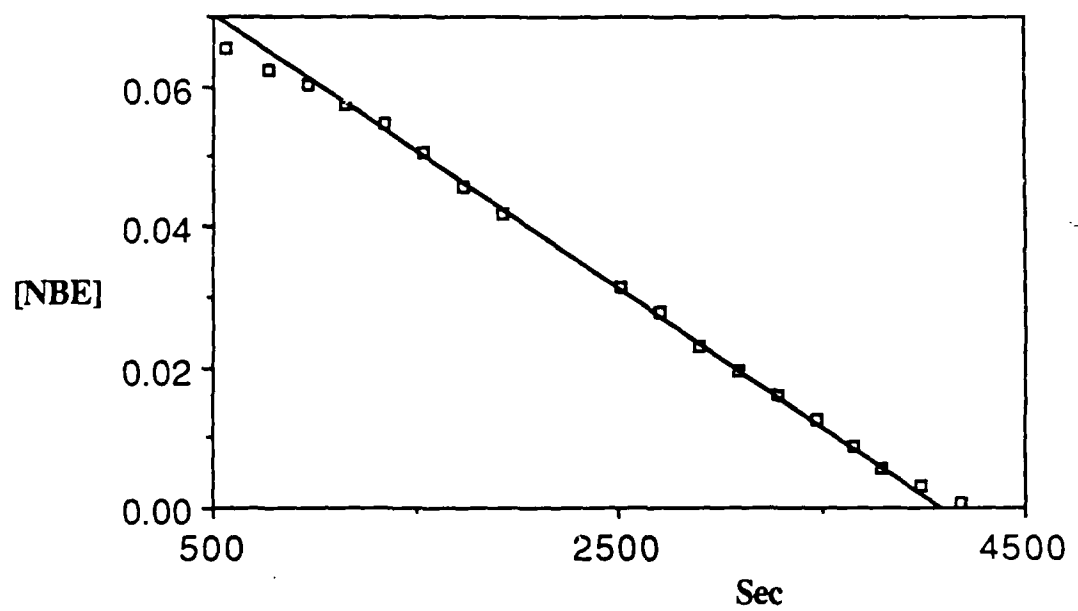


Fig. 8

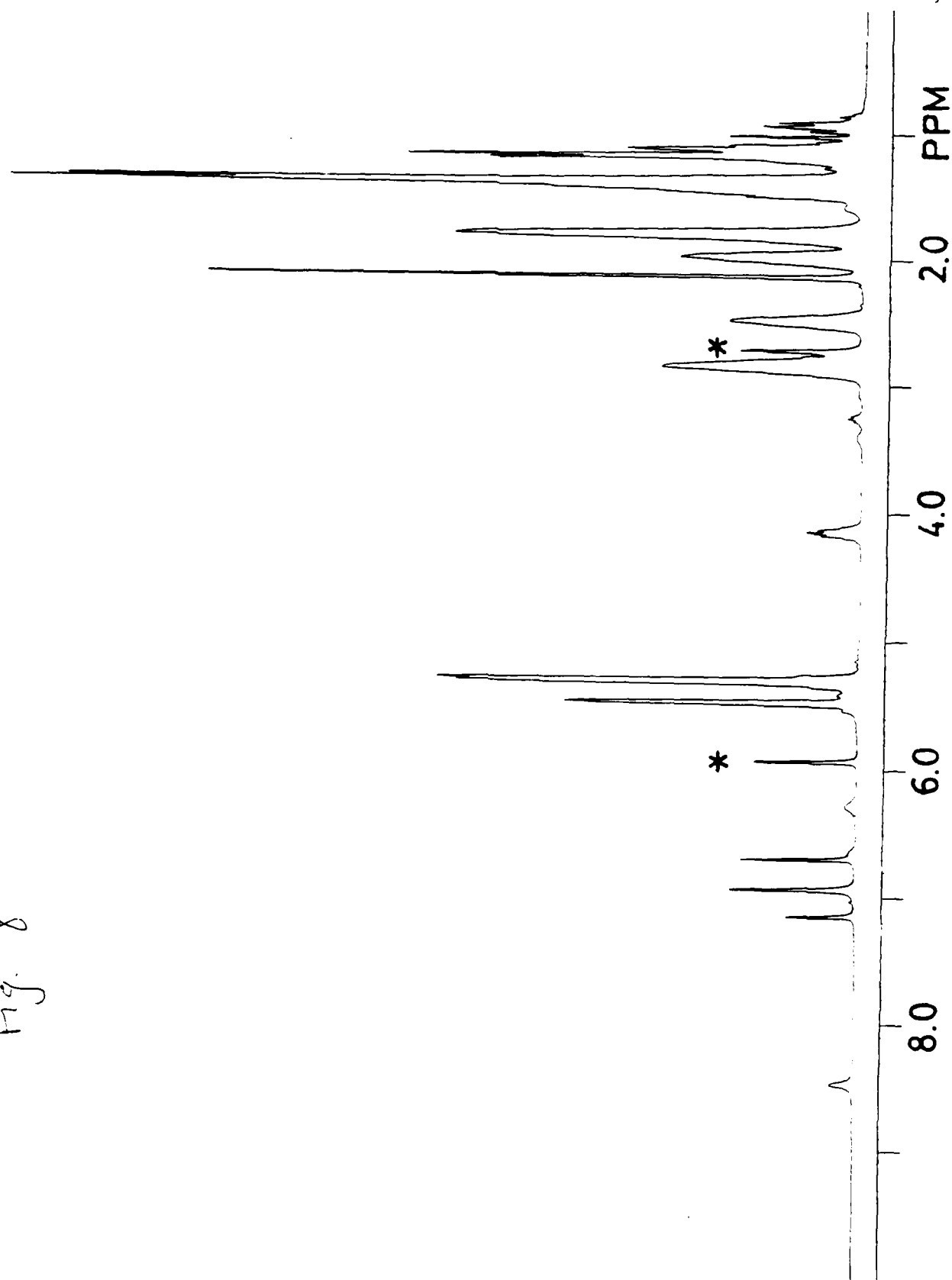
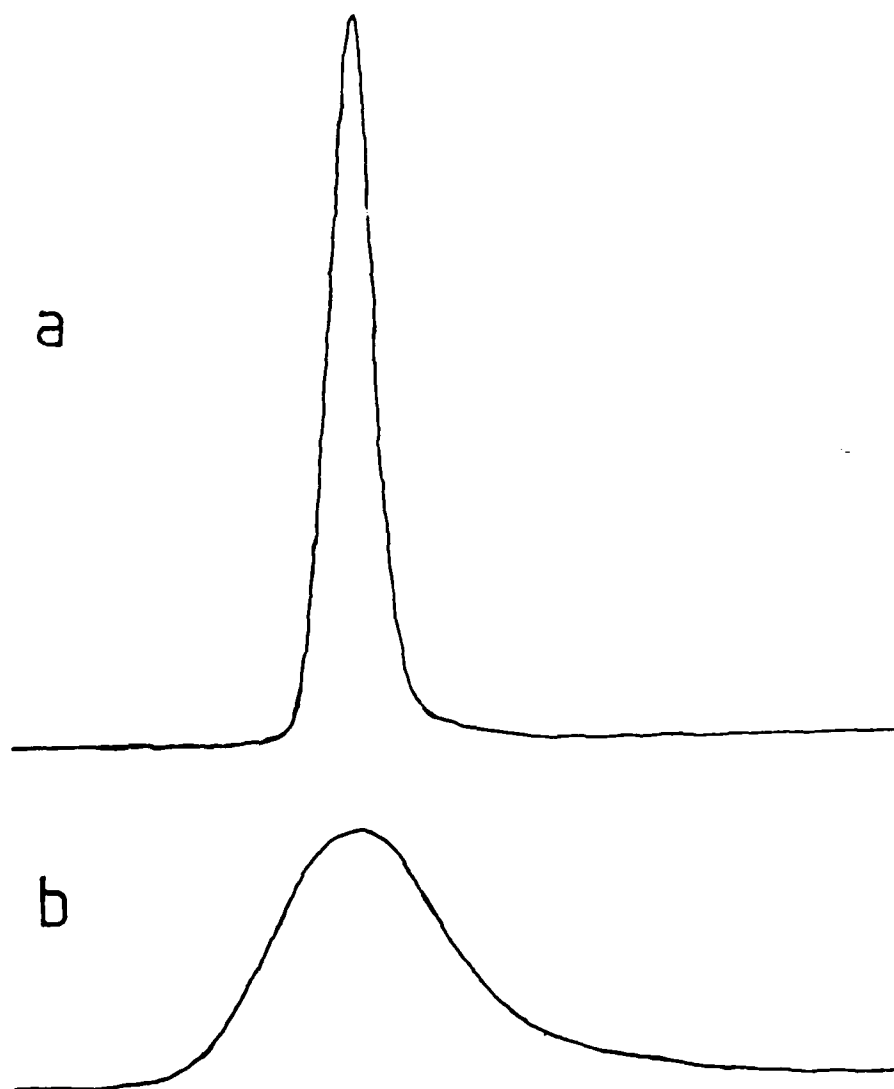


Fig. 9



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